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Physico-Chemical Properties of Regosols in Bulgaria

Biser Hristov

N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection

1331 Sofia, 7 Shosse Bankya str.
Corresponding Author: Biser Hristov, e-mail: bisseru@gmail.com

Abstract

The paper deals with physico-chemical properties of Regosols in Bulgaria. Ten soil profiles are studied in North and South part of the country. These soils are spread mainly on unconsolidated rocks (regolith), slopes and eroded terrains in semi-arid areas. Sediments in these areas are manly alkaline with good sorption capacity. Regosols are moderately acidic to slightly alkaline soils. Exchangeable Ca^{2+} is almost equal to the soil cation exchange capacity. The amount of exchangeable Ca^{2+} is between 8 to 26 mequ/100g. Regosols have high base saturation from 75 to 100 %.

Key words: Regosols, Soil pH, CEC, Base Saturation

Introduction

In Bulgaria weak developed soils such as Regosols are formed mainly on unconsolidated rocks (Regoliths), slopes and eroded terrains usually in semi-arid areas. They are characterized with a weak process of soil formation, shallow profile with primary AC structure, as well as no diagnostic horizons. Regosols development is totally influenced by the properties of parent material. Sediments in these areas are manly alkaline with good sorption capacity. The main component that determine the soil reaction in these soils are carbonates (Hristov, 2014). The soil profiles contain high amounts of calcium carbonate, which increase in depth due to alkaline parent material. Carbonate minerals, such as calcite ($CaCO_3$), aragonite, and dolomite ($CaMg(CO_3)_2$), are considered to be the main sources for alkaline reaction of soils. Calcium and magnesium ions predominate in studied soils and respectively in their cation exchange capacity (CEC). Organic matter in Regosols is low (under 1 %) and CEC depends mainly from clay minerals content and composition. Well known fact is that CEC is the soil's ability to hold positively charged ions. This important soil property impacts soil reaction, soil structure stability, nutrient availability, and the soil's reaction to fertilizers and other ameliorants (Hazleton and Murphy 2007). Cations from the soil surface can be quite easily exchangeable with the cations from the solution (Tomašić et al.2013).In Bulgaria Regosols are slightly alkaline to medium acidic soils with pH form 8.2 to 5.2.

Many methods have been proposed for measuring CEC and exchangeable cations (ISO 11260, ISO 11464; Gillman, G. P. 1979; Sparks et al. 1996; Sumner et al. 1996). The most frequently used methods are based on soil cation exchange with solution of known concentrations of salts which contain cations that are not present in soil. In this study we use the method of Ganev et al. (1980), in which exchangeable ions were determined, titrimetrically and complexometrically, respectively, after saturation of the soil sample with buffer solution (Na-acetate and K-maleate, pH(H_2O) 8.2).

The aim of this paper is to determine the cation exchange capacity, as well as the content of exchangeable cations (Ca^{2+}, Mg^2+, Al^{3+} and $H_{8.2}{}^{+}$), soil pH and base saturation of Bulgarian Regosols and the relationships between them.

Foto 1. *Typical hilly relief in North Bulgaria.*

Material and Methods

Ten soil profiles were studied. Three of them are form South Bulgaria (profile 1,2 and 501) the rest of them are form northern part of the country.

According to WRB2014 classification and location soil profiles are: Profile 1, Calcaric Regosol (Loamic Ohric) in v. Vinogradi, (Teoharov, 2009); Profile 2, Calcaric Regosol (Loamic Ohric) in v. Melnik, (Teoharov, 2009); Profile 501, Calcaric Regosol (Loamic Ohric) in v. Sklave, (Teoharov, 2009); Profile 4, Eutric Regosol (Loamic), in v. Yakimovo; Profile 5, Eutric Regosol (Loamic) in v, Yakimovo; Profile 11, Calcaric Regosol (Siltic, Ohric) in v. Musalievo; Profile 14, Calcaric Regosols (Siltic, Ohric) in v. Milkovitza; Profile 15, Calcaric Regosol (Siltic, Ohric) in v. Milkovitza; Profile 16, Eutric Regosol (Arenic, Ohric) in v. Milkovitza; Profile 18, Calcaric Regosol (Loamic, Ohric) v. Opanetz.

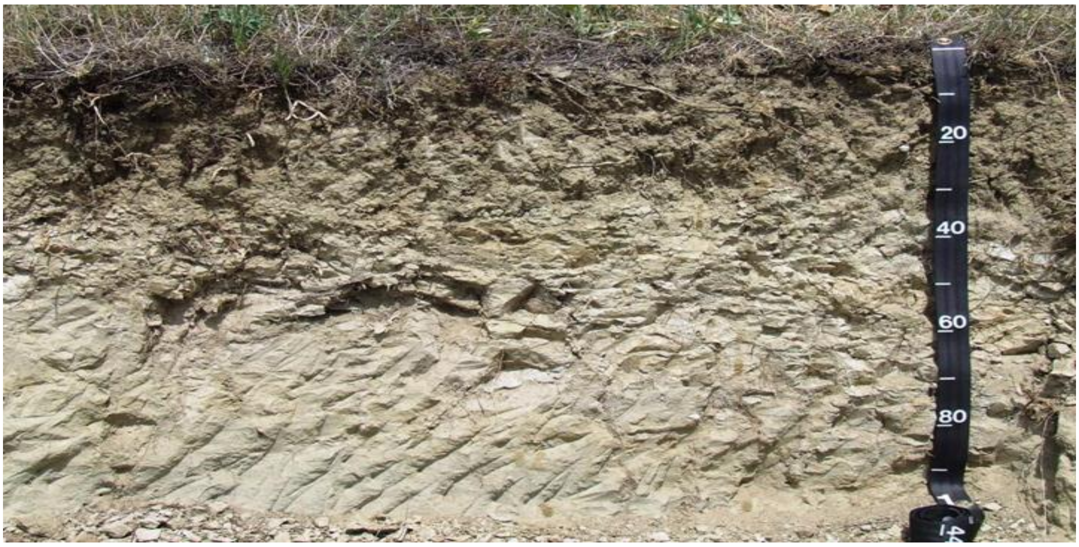

Foto 2. *Profile 1, over Pliocene sediments, village of Vinogradi, South Bulgaria*

The main diagnostic soil characteristics were obtained using the following methods: Soil pH was measured in water suspension 1:2.5. The exchangeable Al^{3+} was determined titrimetrically after displacement of Al^{3+} ions by 1N CaCl2. The total exchangeable hydrogen exch. $H_{8.2}^{+}$ (total acidity) and exchangeable bases (Ca^{2+} and Mg^{2+}) were determined, titrimetrically and complexometrically, respectively, after saturation of the soil sample with buffer solution (Na-acetate and K-maleate, $pH_{(H2O)}$ 8.2). The cation exchange capacity (CEC) was calculated by the sum of $H_{8.2}^{+}$ and exchangeable bases in mequ/100g method of Ganev et al. (1980). Base saturation is the percentage of CEC that is saturated with base exchangeable cations (Ca2+ and Mg2+), V%=Σsum of base exchangeable cations/CEC*100. For statistical analyses and graphics was used Microsoft Excel 2010 software.

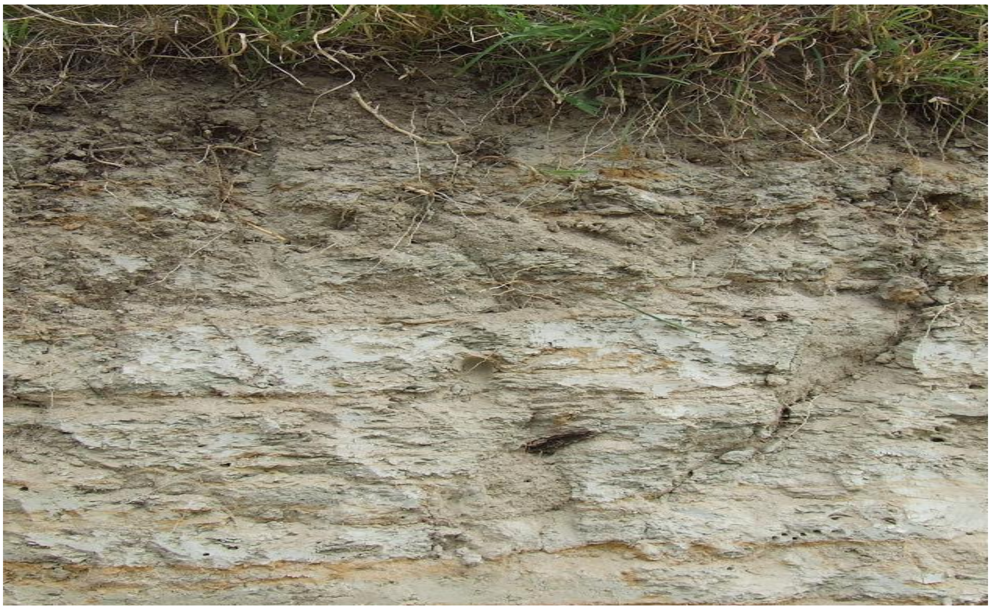

Foto 3. *Profile 18, over quaternary loess, village of Opanetz North Bulgaria*

Results and Discussion

According to analyzed soil samples in Table 1, Regosols are moderately acidic to slightly alkaline soils with pH$_{(H2O)}$ form 5.2 to 8.2, with mean value 7.18 and median 7.6 (table 2) . These soils could have lower pH in mountains regions especially under conifer vegetation. Our soil profiles are spread manly over calcareous sediments with alkaline reactions but in some high steeply places carbonates are washed by rainfalls and consequently the pH is lower such as in profile 16. Statistical correlation matrix (table 3) shows that soil pH correlate mostly with base saturation (0.95) and it has strong correlation with exchangeable Ca^{2+} (0.63).

Table1. *Soil pH (H2O), CEC, Exchangeable Ca^{2+}, Mg^{2+}, H$_{8.2}$$^{+}$, Al^{3+}, Base Saturation*

Horizon / Depth (cm)	**pH/ H$_2$O**	**CEC**	**Ex. H$_{8.2}$$^{+}$**	**Ex. Al^{3+}**	**Ex. Ca^{2+}**	**Ex. Mg^{2+}**	**Base Saturation %**
		mequ/100g					
Profile 1. Calcaric Regosol (Loamic Ohric), (Teoharov, 2009)							
A$_k$ 0 – 17	7.5	24.49	0.0	0.0	23.14	1.35	**100**
AC$_k$ 17 – 30	8.0	25.48	0.0	0.0	24.98	0.50	**100**
C$_k$ 30 – 50	8.3	19.04	0.0	0.0	18.30	0.74	**100**
Profile 2. Calcaric Regosol (Loamic Ohric), (Teoharov, 2009)							
A$_1$ 0 – 17	6.7	15.46	2.11	0.0	9.40	3.95	**86.35**
C$_1$ 17 – 30	7.7	16.94	0.0	0.0	14.84	2.10	**100**
Profile 501. Calcartic Regosol (Loamic Ohric), (Teoharov, 2009)							
A$_k$ 0 – 20	8.0	22.00	0.80	0.0	17.60	3.60	**96.40**
C$_k$ 20 – 47	8.2	15.70	0.50	0.0	12.20	3.20	**96.80**
Profile 4. Eutric Regosol (Loamic)							
A$_h$ 0 – 14	6.0	22.0	4.5	0.0	15.0	2.3	**79.55**
C$_K$ 14 - 30	5.8	20.8	5.0	0.5	13.2	2.5	**75.96**
Profile 5. Eutric Regosol (Loamic)							
A$_k$ 0 - 20	5.8	21.0	4.8	0.4	13.0	2.8	**77.14**
C$_k$ 20 – 40	5.2	20.1	5.2	0.9	12.4	2.6	**74.13**
Profile 11. Calcaric Regosol (Siltic, Ohric)							
A$_k$ 0 – 18	7.9	24.8	0.0	0.0	21.5	3.3	**100**
C$_k$ 18 – 35	8.3	24.7	0.0	0.0	21.2	3.5	**100**
Profile 14. Calcaric Regosols (Siltic, Ohric)							
A$_k$ 0 – 10	7.6	29.0	0.0	0.0	26.0	3.0	**100**
AC$_k$ 10 – 32	7.8	25.4	0.0	0.0	22.0	3.4	**100**
Profile 15 Calcaric Regosol (Siltic, Ohric)							
A$_h$ 0 – 16	6.4	23.9	3.5	0.0	17.5	3.0	**85**
C$_k$ 16 –35	7.4	20.0	0.0	0.0	16.8	3.0	**100**
Profile 16. Eutric Regosol (Arenic, Ohric)							
A$_h$ 0 – 15	5.5	15.0	3.2	0.5	10.5	1.2	**78.67**
C$_1$ 15 – 30	6.5	9.9	0.8	0.0	8.0	1.0	**91.92**
Profile 18. Calcaric Regosol (Loamic, Ohric)							
A$_k$ 0 – 14	8.1	25.9	0.0	0.0	22.6	3.3	**100**
C$_k$ 14 – 30	**8.0**	**21.9**	**0.0**	**0.0**	**18.5**	**3.4**	**100**

Studied soils have average cation exchange capacity (Mean=21 mequ/100g) with values between 9.9 to 29 mequ/100g. The fact is that profiles 16 with lowest CEC and profile 14 with highest are spread over loess in North Bulgaria, but profile has sandy (arenic, WRB 2014) texture with low clay content (Hristov, 2014).

Similar CEC have Calcic Chernozems in North Bulgaria spread also over loess between 29 to 20 mequ/100g (Ganev et al. 1990) . Higher CEC in Bulgaria have Vertisols, Haplic Chernozem, Phaeozems and other caly rich soils (Ganev et al., 1990; Nikova et al., 2011; Hristova et al., 2002). Sandy and shallow soils such as Cambisols, Arenosols and Leptosols have lower CEC and base saturation (Andreeva, 2014; Kirilov et al., 2015).

Accodring Malinova (2016) Regosols in Central Balkan mountain have CEC between (47 – 4, cmol(+).kg^{-1}). In this mountain area CEC depends also form parent rock. The soils developed on weathering materials of gneiss and granite have higer CEC and Base Saturation than and those developed on white gneiss and schist.CECs correlate totally and only with exchangeable calcium (0.90) because in most of the soil profiles exch. Ca^{2+} is almost equal to the soil CEC, and all other cations are in low quantities (Figure 1). Calcium is the most plentiful cation occupying 75% or more of the sites on the cation exchange complex of soil that is neutral to slightly acidic. Calcium is adsorbed strongly as compared with other exchangeable cations.(Ganev, 1990, Sposito, 1989, Benkova et al., 2003)

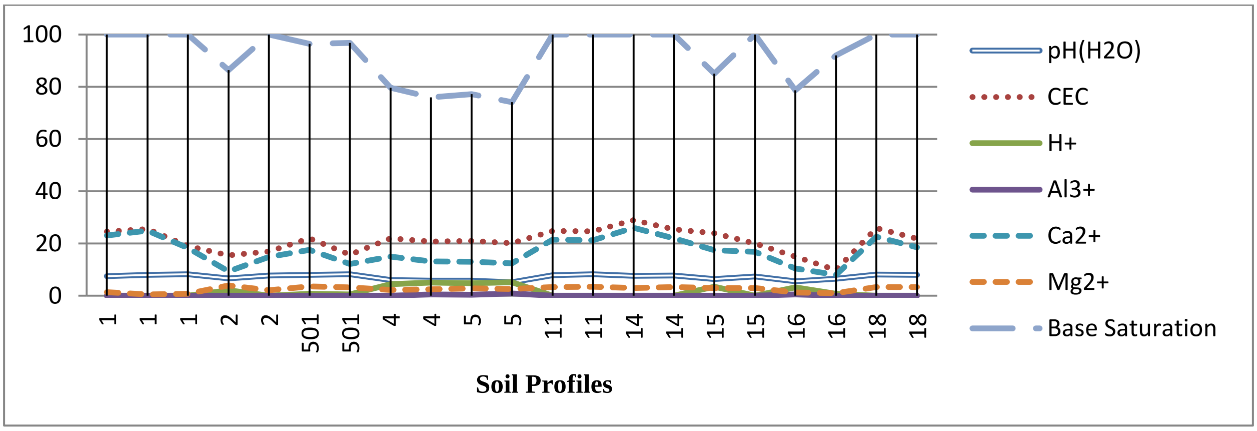

Figure 1. *Graphical distribution - soil pH, CEC, Exchangeable* Ca^{2+}, Mg^{2+}, H^{+}, Al^{3+}, *Base Saturation*

Calcium is also found in the silt particle size fraction. That is why soils with more clay adsorb more calcium. This is particularly the case in loess and quaternary sediments (Hristov et al., 2010). As it was mentioned above carbonate minerals, such as calcite ($CaCO_3$), aragonite, and dolomite ($CaMg(CO_3)_2$), are considered to be the main sources for exch. Ca^{2+} in soil. The amount of exch. Ca^{2+} varies from 8 to 26 mequ/100g . Correlation matrix (Table 3) shows that exchangeable calcium correlates well with other data. In addition to strong correlation between CEC and soil pH, there is also good relation with base saturation (0.66).

Other exchangeable basic cation such as Mg^{2+} also could be found in sediments and carbonate minerals like dolomite. The behavior of magnesium in soil is similar to calcium. Regosols and other soils often contain less magnesium relative to calcium. This is because a magnesium ion is not adsorbed as tightly by clay particles and organic colloids (Rytwo et al. 1996). In general, the source of magnesium in regolith is less than that for calcium. As an exchangeable cation in neutral to slightly acidic soil, magnesium is commonly second in abundance to calcium. In studied profiles the amount of exchangeable Mg^{2+} is between 0.5 to 3.95 mequ/100g.

In contrast to other cations like K, Ca, and NH^{4+}, Mg is less mobile in soils. Whereas the ionic radius of Mg is smaller than that of Ca, K or Na, its hydrated radius is substantially larger (Shaul 2002; Gardner2003; Maguire et al. 2002). One consequence is that Mg is less strong bound to soil charges (CEC) leading to compared to other cations higher Mg concentrations in the soil solution (Gransee et al. 2013). That is one of the reasons why Mg^{2+} doesn't correlate with CEC, Ca^{2+}, ect.

Table 2. *Descriptive statistic - soil pH, CEC, Exchangeable Ca^{2+}, Mg^{2+}, $H_{8.2}^{+}$, Al^{3+}, Base Saturation*

	pH(H2O)	***CEC***	***$H_{8.2}^{+}$***	***Al^{3+}***	***Ca^{2+}***	***Mg^{2+}***	***Base Saturation***
Mean	7,18	21,12	1,45	0,11	17,08	2,56	92,47
Maximum	8,3	29	5,2	0,9	26	3,95	100
Minmum	5,2	9,9	0	0	8	0,5	74,13
St. Dev.	1,03	4,58	2,00	0,25	5,22	1,03	9,88
Median	7,6	21,9	0	0	17,5	3	100

Chemical index of total acidity of soils ($H_{8.2}^{+}$) is the sum of all exchangeable cations with acidic functions, adsorbed on strongly acid and weekly acid ion exchangers of the soil colloids (Ganev, 1989). Total acidity in studied soils is low, from 0 to 5.2 mequ/100g. The reason for that are carbonates with high pH in parent rocks as it was mentioned above. Thus, total acidity of the soils shows inverse correlation with soil pH, Base Saturation, exchangeable Ca^{2+} and it has positive correlation only with soil exchange acidity (exch. Al^{3+}).

Table 3. *Correlation matrix - soil pH, CEC, Exchangeable Ca^{2+}, Mg^{2+}, $H_{8.2}^{+}$, Al^{3+}, Base Saturation*

	pH(H2O)	***CEC***	***$H_{8.2}^{+}$***	***Al^{3+}***	***Ca^{2+}***	***Mg^{2+}***	***Base Saturation***
pH(H2O)	1,00						
CEC	0,35	1,00					
H^{+}	-0,91	-0,20	1,00				
Al^{3+}	-0,76	-0,19	0,75	1,00			
Ca^{2+}	0,63	0,90	-0,56	-0,43	1,00		
Mg^{2+}	0,15	0,28	0,00	-0,11	0,05	1,00	
Base Saturation	0,95	0,32	-0,98	-0,78	0,66	0,05	1.00

Soil exchange acidity (exch. Al^{3+}) is the acidity of the strongly acid positions of soil adsorbent (exchange aluminum, manganese, zinc etc., amphoteric cations and eventually hydrogen ions)(Ganev, 1989). In the studied soil profiles exch. acidity is too low almost zero and it has no influence on soil properties.

The sum of basic exchange cations expressed in per cent (%) of the value of total CEC is the degree of base saturation. Regosols have high base saturation between 75 – 100 % due to high amount of exch. Ca^{2+} and in addition exch. Mg^{2+}. According to correlation matrix base saturation has strong positive correlation with soil pH and exch. Ca^{2+}. Otherwise it has inverse correlation with soil total acidity ($H_{8.2}^{+}$) and exchange acidity (exch. Al^{3+}).

Conclusion

Regosols in Bulgaria are spread manly over calcareous sediments with alkaline reaction. They are moderately acidic to slightly alkaline soils with $pH_{(H2O)}$ form 5.2 to 8.2. Studied soils have cation exchange capacity with values between 9.9 to 29 mequ/100g. CEC correlate totally and only with exchangeable calcium (0.90), because in these soils exch. Ca^{2+} is almost equal to soil CEC. Loess and other quaternary sediments are considered to be the main sources for exch. Ca^{2+} of the soils. The amount of exch. Ca^{2+} vary from 8 to 26 mequ/100g . Regosols contain less magnesium relative to calcium because magnesium ion is not adsorbed as tightly by clay particles and organic colloids. In studied profiles the amount of exchangeable Mg^{2+} is between 0.5 to 3.95 mequ/100g . Total acidity and exchange acidity are in low quantities and the reason for that is high base saturation form 75 to 100 %.

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Nutritional Value of Cowpea (*Vigna Unguiculata* L. Walp) Grain Grown Under Different Soil Moisture as Affected to the Dual Inoculation with Nitrogen Fixing Bacteria and Arbuscular Mycorrhizal Fungi

Ira Stancheva*, Kostadinka Nedyalkova, Maria Geneva*,**
Radka Donkova, Marieta Hristozkova*,**
Ionita Perfanova, Mariana Sichanova* , Galina Petkova**,**
Efrosina Djonova, Hristo Valchovski****
** Institute of Plant Physiology and Genetics, Bulgarian Academy of Sciences,*

1113 Sofia, Bulgaria

***N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection*

1331 Sofia, 7 Shosse Bankya str.

Corresponding Author: Ira Stancheva, e-mail: ira_stancheva@abv.bg

Abstract

The study was performed to evaluate the nutritional value and antioxidant properties of cowpea grain, where plants were grown under conditions of tripartite symbiosis (cowpea plants, nitrogen-fixing bacteria (*Bradyrhizobium japonicum*) and arbuscular mycorrhizal fungi, (*Glomus intraradices*) without fertilization. Cowpea plants (*Vigna unguiculata* (L.) Walp) cv. Hrisi were grown in a glasshouse until the full maturity of grain on the Alluvial meadow soil (Eutric Fluvisol) at three levels of water-holding capacity (40, 60 and 80%). *Bradyrhizobium japonicum* solely and in combination with arbuscular mycorrhizal fungi increased the content of proteins, soluble sugars and total phenols in the cowpea seeds. When dual inoculation has applied the levels of proteins and soluble sugars in the cowpea grain did not reduce at 40%, nor at 80% in comparison with the optimal water-holding capacity level (60%). Antioxidant capacity at 40% water-holding capacity was determined by the increased content of water soluble antioxidants, flavonoid content and increased ferric reducing power activity and increased antioxidant levels was expressed more distinguished in the treatments with dual inoculation. Slight change of antioxidants in the grain of cowpea was established at an elevated level of water supply. Nutritional value of a grain of cowpea after dual inoculation with *Bradyrhizobium* strains and *Glomus intraradices* was not determined by the water-holding capacity levels.

Key words: Arbuscular Mycorrhizal Fungi, Nitrogen-Fixing Bacteria, Nutritional Value, Soil Moisture, *Vigna unguiculata* (L.) Walp

Abbreviations: AM fungi - arbuscular mycorrhizal fungi; DPPH• - diphenylpycril-hydrazyl; FRAP - ferric reducing power; WHC - water holding capacity

Introduction

Cowpea (*Vigna unguiculata* L. Walp) is a widely grown legume food crop of the tropics and sub-tropics, used in the diets of humans and other mammals. Cowpea seeds are an excellent source of carbohydrate (50–60%) and an important source of protein (18–35%). They also contain an appreciable quantity of micronutrients such as vitamin A, iron and calcium (Prinyawiwatkul et al., 1996). The crude protein from the seed and leaves ranges, respectively between 23 and 32% (Diouf, 2011). Polyphenolic compounds are also found. They can interact with proteins and reduce their digestibility, as well as alter organoleptic and functional properties of the seed flour (Okafor et al., 2002). Polyphenolic compounds also have beneficial effects due to their antioxidant activity which is fundamental to the life. (Rice-Evans et al., 1997). Recently, the ability of phenolic substances including flavonoids and phenolic acids to act as antioxidants has been extensively investigated (Rice-Evans et al., 1997). On the other hand vitamin C, *a*-tocopherol and phenolic compounds, which are present naturally in vegetables, fruits and grains, possess the ability to reduce oxidative damage associated with many socially significant diseases, including cancer, diabetes and cardiovascular diseases (Lee et al., 2000).

During the last years, the role of microorganisms in the conservation of soil fertility increased. Vessey (2003) pointed out that the soil microorganisms were successfully applied as biofertilizers, useful to substitute chemical fertilization. The arbuscular mycorrhizal fungi (AMF) and nitrogen-fixing bacteria have an important role in plant nutrient uptake, not only for the availability of P and N but also of other nutrients such as K, Ca and Mg (Clark and Zeto, 2000). The effectiveness of the tripartite symbiosis – AM fungi, *Bradyrhizobium*, and legumes plant, depends on the competition of the three symbionts for carbon.

Therefore, the present study was aimed at evaluating the nutritional compounds (crude protein and sugars) of the grains of cowpea, grown under conditions of tripartite symbiosis without fertilization, their phenolic constituents, antioxidant compounds and free radical scavenging capacity.

Material and Methods

Growth conditions and treatments

Cowpea plants (*Vigna unguiculata* (L.) Walp) cv. Hrisi, created in the Bulgarian Institute for Plant Genetic Resources "K. Malkov " were grown in a glasshouse until the full maturity of grain using Alluvial meadow soil (Eutric Fluvisol) (IUSS Working Group WRB, 2006). The agrochemical characteristics of the soil are as follows: pH (H_2O) - 7.4; mineral N - 19 mg kg^{-1} soil; P (P_2O_5) – 99 mg kg^{-1} soil, K (K_2O) – 334 mg kg^{-1} soil. Water was added to make up about 40%, 60% and 80% of water-holding capacity (WHC). An inoculum of AM fungi, *Glomus intraradices* EEZ 01 was used. It was added to the soil (at 2 cm depth under soil surface) before sowing in quantity 0,5 g per pot. The mycorrhizal strain was provided from the AMF collection of Estacion Experimental del Zaidin (CSIC Granada, Spain). The seeds before sowing were inoculated with the bacterial suspension of *Bradyrhizobium japonicum*, strains 273 and 269 at approximately 10^8 cells per cm^3. The tested strains are from the collection of Soil Microbiology Department of Nicola Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection, Bulgaria.

The following scheme was used per each level of water holding capacity:
1. Control plants
2. Plants inoculated with *Br. japonicum*-273
3. Plants inoculated with *Br. Japonicum*-269
4. Plants inoculated with *Gl. intraradices* EEZ 01
5. Plants inoculated with *Br. japonicum*-273 + *Gl. intraradices* EEZ 01
6. Plants inoculated with *Br. japonicum*-269 + *Gl. intraradices* EEZ 01

Content of total proteins and soluble sugars

The extraction of proteins from cowpea grain was carried out following the method of Mirkov et al. (1994). 0.1 g of finely grounded grains flour were extracted in the extraction buffer (10 mM Tris-HCL (pH 7.5), 500 mM NaCl, 1% 2-mercapto-ethanol, 0.1% Triton-X-100, 2 mM phenylmethylsulphonyl fluoride (PMSF) (1 ml/ml sample) by homogenization followed by incubation at 4°C for 1 h, and then centrifuged at 15,000 rmp for 15 min at 4°C. The supernatant was collected and stored frozen in aliquots. The protein content in the crude extracts was determined by the method described by Bradford (1976) using bovine albumin as standard. The seeds were analyzed for soluble sugars via refractometer.
Soluble sugars were expressed in percents.

Antioxidant capacity and antioxidant metabolites

Free radical scavenging activity was measured from the bleaching of the purple methanol solution of free stable radical (diphenylpycril-hydrazyl, $DPPH^{\bullet}$), according to Tepe et al. (2006). $DPPH^{\bullet}$ is a stable radical with a maximum absorption at 517 nm that can readily undergo reduction by an antioxidant. The percent inhibition of the $DPPH^{\bullet}$ radical (I%) was calculated by the following equation:

$I\% = (A_{blank} – A_{sample}/A_{blank}) \times 100$,

where A_{blank} is the absorbance of the control reaction (containing all reagents except the test compound), and A_{sample} is the absorbance of the test compound, i.e. cowpea grain extracts.

Ferric reducing power (FRAP assay) The FRAP reagent was freshly prepared by mixing acetate buffer (300 mM, pH 3.6), TPTZ solution (10 mM TPTZ in 40 mM HCl), and $FeCl_3$–$6H_2O$ (20 mM) in a ratio of 10:1:1 (Benzie et al., 1996). To perform the assay, 900 mL of FRAP reagent, 90 mL of distilled water and 30 mL of the plant extract were mixed and incubated at 37°C for 15 min. The absorbance was measured at 595nm using the FRAP working solution as a blank. The antioxidant potential of samples was determined from a standard curve, plotted using the $FeSO_4.7H_2O$ linear regression. The results were corrected for dilution and expressed as mmol of Fe^{2+} g^{-1} of dried sample.

For determination of total phenols and flavonoids grain samples (1 g) were ground and exhaustively extracted with 96% (v/v) methanol. Concentrations of phenolic compounds were determined spectrophotometrically using Folin–Ciocalteu reagent and calculated as caffeic acid equivalents (Pfeffer et al., 1998). Flavonoids in plant tissues were measured spectrophotometrically according to Zhishen et al. (1999), using the standard curve of catechin.

Spectrophotometric quantification of water-soluble and lipid-soluble antioxidant capacity, expressed as equivalents of ascorbate and α-tocopherols were performed through the formation of phosphomolybdenum complex (Prieto et al., 1999). The assay was based on the reduction of Mo (VI) to Mo (V) by the sample analysis and the subsequent formation of a green phosphate/Mo (V) at acidic pH. 0.5 g plant dry material was ground with pestle and mortar to a fine powder. 3ml dH_2O was added and the suspension was homogenized, transferred to tubes and shaken for 1 h at room temperature in dark. The suspension is filtered and extraction is repeated with 3 ml dH_2O. The pellet was washed again with 2 ml dH_2O. For lipid soluble antioxidant capacity (expressed as α-tocopherols), the procedure is the same except the extraction is carried out with hexane as a solvent. The method has been optimized and characterized with respect to linearity interval, repetitively and reproducibility, and molar absorption coefficients for the quantitation of water-soluble and lipid-soluble antioxidant capacities, expressed as equivalents of ascorbate, and α-tocopherols (Prieto et al., 1999) Absorption coefficients were: (3.4±0.1) x103 M^{-1} cm^{-1} for ascorbic acid and (4.0±0.1) x103 M^{-1} cm-1 for α-tocopherols.

Statistical Analyses

Data are expressed as means ± standard error where $n = 3$. Comparison of means was performed by the Fisher LSD test ($P \leq 0.05$) after performing multifactor ANOVA analysis. A statistical software package (StatGraphics Plus, version 5.1. for Windows, USA) was used.

Results

Under conditions of optimal soil moisture (60% WHC) the protein content as well as the content of the soluble sugars in cowpea grains were affected in a similar way at the experimental treatments. Inoculation with *Br. japonicum*-273 resulted in those parameters increase (Figure 1). On the other hand combined treatment with AM fungi and the other *Bradyrhizobium* strain - 269 affected more favorably protein content and soluble sugars in cowpea grains.

Br. japonicum-273 solely and in combination with AM fungi increased the content of total phenols. Single inoculation with AM fungi significantly increased flavonoids in cowpea grain (Figure 1). Water-soluble and lipid-soluble antioxidant capacity expressed as equivalents of ascorbate and α-tocopherols respectively was measured to be the higher as a result of inoculation with *Br. japonicum*-273. Despite the free radical scavenging activity did not differ among the treatments, ferric reducing power activity (FRAP assay) increased in the grain in plants inoculated with both *Bradyrhizobium* strains as well as at the treatments with dual inoculation (*Bradyrhizobium* strain + *Gl. intraradices).*

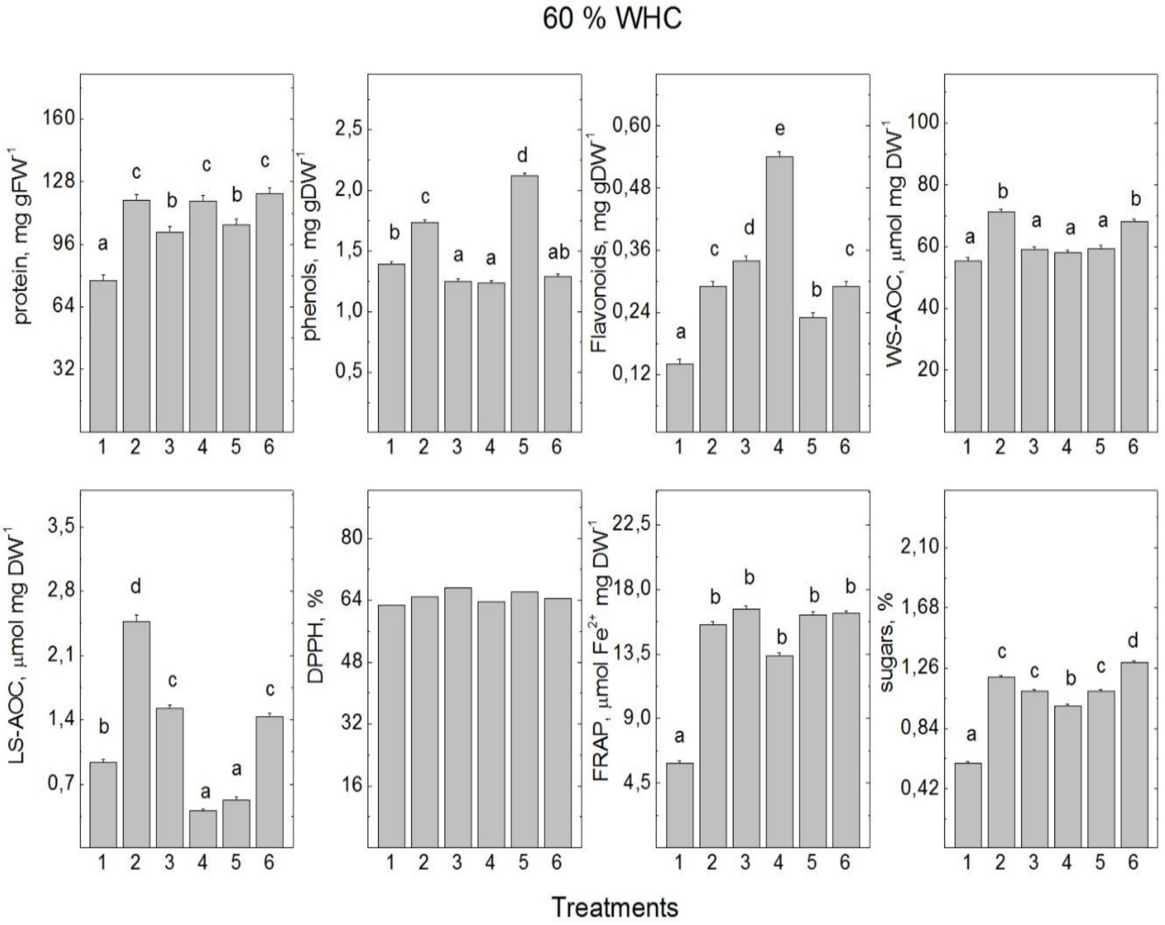

Figure 1. *Nutritional properties and metabolites with antioxidant activity of Vigna unguiculata grain at 60% water holding capacity. Different letters in the values indicate significant differences assessed by Fisher LSD test (P ≤ 0.05) after performing ANOVA analysis*

Under 40% WHC total protein content decreased only in the grain from the treatments with single inoculation with *Br. japonicum*-269 and *Gl. intraradices* EEZ 01 (Figure 2). Dual inoculation with AM fungi and *Bradyrhizobium* strains did not result in protein reduction under drought conditions in comparison with the optimal level of water-holding capacity-60%. Soluble sugars increased in the grain of cowpea grown at 40% WHC. Phenolic content slightly decreased with the exception of the grain from the treatment with AM fungi and *Br. japonicum*-269. Flavonoids rose after inoculation with fungi and combined inoculation with *Bradyrhizobium* strains and *Gl. intraradices*. Under drought conditions, 40% WHC water soluble antioxidants increased while lipid-soluble antioxidants are reduced. Radical scavenging activity was strongly reduced where *Br. japonicum*-269 was applied solely and combination with AM fungi while FRAP activity remained higher in all experimental treatments.

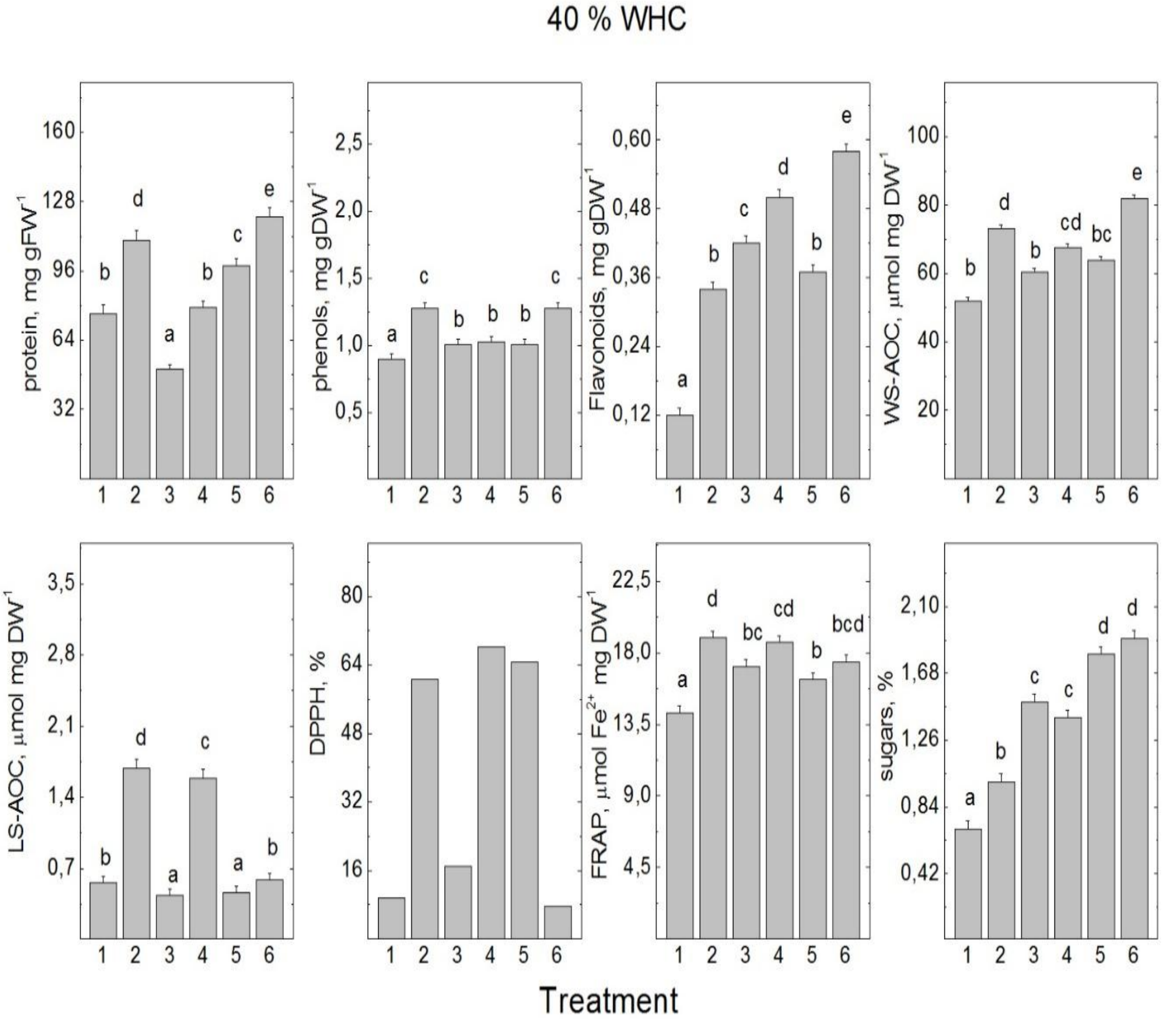

Figure 2. *Nutritional properties and metabolites with the antioxidant activity of Vigna unguiculata grain at 40% water holding capacity. Different letters in the values indicate significant differences assessed by Fisher LSD test (P ≤ 0.05) after performing ANOVA analysis*

At increased water holding capacity level (80% WHC), protein content increased significantly compared with the treatments from the optimal level as a result of *Bradyrhizobium* strains application solely and in combination with *Gl. intraradices* (Figure 3). Soluble sugars also increased in the grain of cowpea after mycorrhization and dual inoculation. Phenols decreased as compared to the treatments with optimal water supply, but flavonoids remained higher as a result of mycorrhization and dual inoculation. Water - soluble and lipid - soluble antioxidants did not rise under waterlogging conditions.

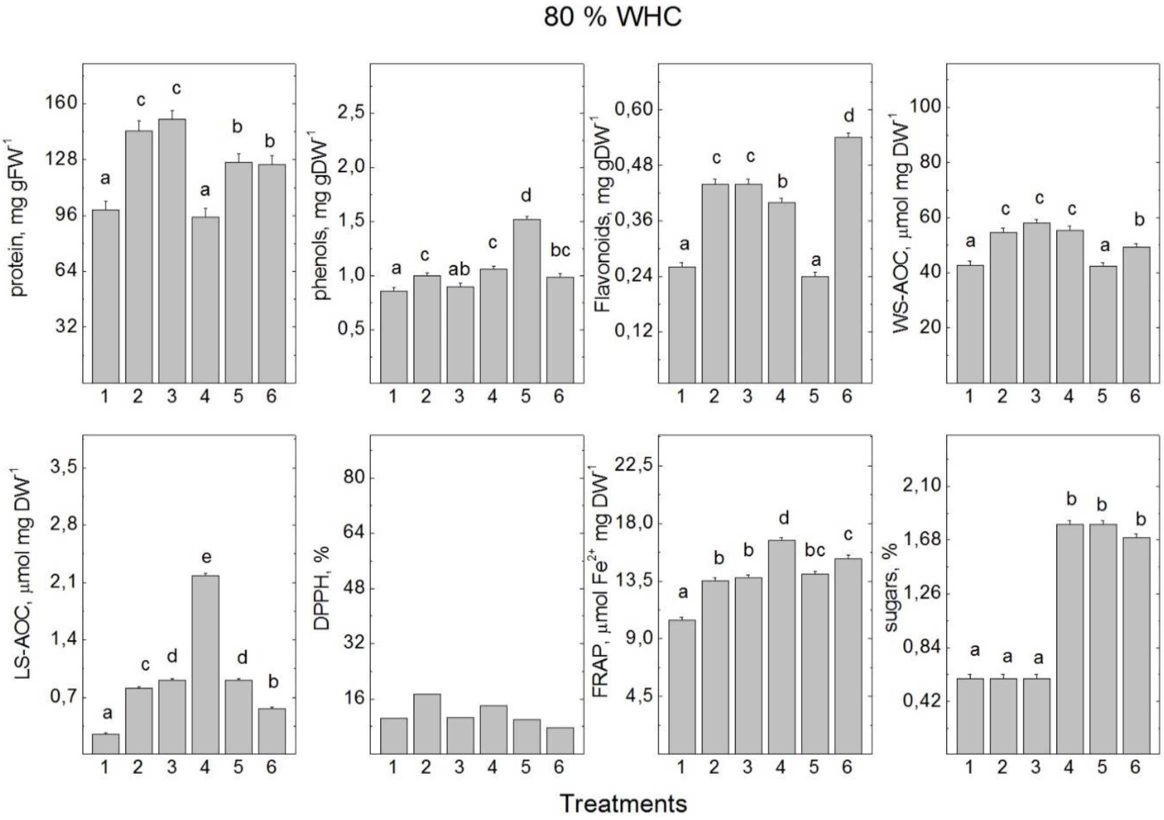

Figure 3. *Nutritional properties and metabolites with the antioxidant activity of Vigna unguiculata grain at 80% water holding capacity. Different letters in the values indicate significant differences assessed by Fisher LSD test (P ≤ 0.05) after performing ANOVA analysis*

Discussion

At 60% WHC protein content of cowpea grain was in the range 77.31 -121.96 mg.g^{-1} which is 7.7-12.2%. The level of soluble sugars in the cowpea grain at 60% WHC was in the range 0.6-1.3%. Cowpea seeds are an excellent source of carbohydrate (50–60%) and an important source of protein (18–35%) (Mune et al., 2008). Rivas - Vega et al. (2006) reported that crude protein content of whole raw cowpea is within the range of values reported for other varieties of cowpea - 26.14%). The protein content of cowpea grain obtained from intercropped plots (23.7 to 26.3%) in South Africa was similar to that from sole plots (23.7 to 25.7%) (Sebetha et al., 2010).

Starch is the most abundant carbohydrate in cowpea, while sugars represent only a small percentage (Longe, 1980). The sucrose concentration of seeds is an important component of the taste in cowpea (*Vigna unguiculata* L. Walp.) (Tchiagam et al., 2011). Stachyose (3.43%), sucrose (2.97%) and raffinose (1.24%) are the predominant sugars in nonfermented (control) cowpea flour. Verbascose was not detected in the control flour even after a 35-min elution time. Akpapunam and Markakis (1979) reported sugars from 13 American cowpea varieties to have 3.4% stachyose, 2.2% sucrose, 1.2% raffinose, and 0.9%

verbascose (dry weight basis), while 2.7% stachyose, 1.6% sucrose, 0.7% raffinose, and 3.6% verbascose were reported for 20 Nigerian cowpea varieties (Longe, 1980).

Zia-Ul-Haq et al. (2013) reported that cowpea is rich in polyphenolic compounds more than other leguminous seeds and pulses and phenolic constituents contained in cowpea may have a future role as ingredients in the development of functional foods. It was known that polyphenolic compounds also have beneficial effects due to their antioxidant activity and the ability of phenolic substances including flavonoids and phenolic acids to act as antioxidants has been extensively investigated (Rice-Evans et al., 1997). On the other hand vitamin C, α-tocopherol and phenolic compounds, which are present naturally in vegetables, fruits and grains, directly associated with antioxidant activity (Zia-Ul-Haq et al., 2008). Some authors (Siddhuraju and Becker, 2007) pointed out that the DPPH radical and ABTS cation radical scavenging activities were well proved and correlated with the ferric reducing antioxidant capacity of the cowpea seed extracts.

Antioxidant defense under drought conditions was determined by the increased content of water soluble antioxidants, flavonoid content and increased FRAP activity and increased antioxidant levels was expressed more distinguish in the treatments with dual inoculation. Consequently when dual inoculation was applied the levels of proteins and soluble sugars in the cowpea grain did not reduce under drought in comparison with the control. AM symbiosis alleviates drought stress via direct water uptake and transport through fungal hyphae to the host plants (Augé et al., 2007). The problems caused from drought and its effect on growth, yield and nutritional values were under taken in several studies (Henry, Mather, 2003; Anitha et al., 2004).

Conclusion

At a global scale, the effects of continuous agricultural practices such as fertilization can cause serious damage to the environment. Inoculation is one of the most important sustainable practices in agriculture, because microorganisms establish associations with plants and promote plant growth by means of several beneficial characteristics.

In conclusion neither reduced nor excess water supply did affect nutritional value of grain of cowpea after dual inoculation with *Bradyrhizobium* strains and *Gl. intraradices*. Nevertheless, the beneficial effects of the microsymbionts, observed in this study, arouse an interest in considering the role of rhizobia-AM-plant tripartite symbiosis in affecting nutritional value of cowpea grain grown under different soil moisture. *Bradyrhizobium japonicum* solely and in combination with arbuscular mycorrhizal fungi increased the content of proteins, soluble sugars and total phenols in the cowpea seeds. When dual inoculation has applied the levels of proteins and soluble sugars in the cowpea grain did not reduce at 40%, nor at 80% in comparison with the optimal water-holding capacity level (60%). Slight change of antioxidants level is a precondition for the lack of increase free radical scavenging activity ($DPPH^{\bullet}$) and ferric reducing power (FRAP) in the grain of cowpea grown at elevated level of water supply. Finally, the search for beneficial bacteria is important for the development of new and efficient stimulants for agriculture.

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Geochemical patterns of soils in the Bobov dol valley, Bulgaria. Assessment of Cu, Pb and Zn contents

Venera Tsolova*, Ivona Nikova*, Bisser Hristov*, Kalin Ruskov**, Alexandar Zdravkov**
**N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection*
1331 Sofia, 7 Shosse Bankya str.
***University of Mining and Geology "St. Ivan Rilski",*
Studentski grad, 1700 Sofia, Bulgaria

Corresponding Author: Venera Tsolova, e-mail: venera_tsolova@abv.bg

Abstract

The content of Si, Al, Fe, Ti, Mn, Mg, Ca, Na, K, S, P, C, Cu, Pb and Zn were determined in order to reveal geochemical patterns of soils in the Bobov dol valley, Bulgaria. Since the Bobov dol Thermal-electric Power Plant (TPP) is situated in the valley this paper pays attention to the geospatial distribution of Cu, Pb, and Zn due to their diverse vital significance. Elements assemblages and geospatial distribution pathways are also discussed in the light of the past 40 years of operation of the Thermal Power Plant. According to the results obtained the average content of Cu (27.04 mg kg^{-1}), Pb (21.96 mg kg^{-1}) and Zn (57.95 mg kg^{-1}) is higher than the average content of elements in local soil parent rocks: Cu (20.03 mg kg^{-1}), Pb (6.07 mg kg^{-1}) and Zn (46.60 mg kg^{-1}). Compared to the precautionary threshold concentrations adopted for assessing the soil contamination in Bulgaria the elements contents are lower including their maximum values. However, the geoaccumulation indexes reveal an initial stage of contamination of soils with Pb. Lead tends to follow a separate mode of geospatial distribution which is controlled by both the geogenic factors and the aerosol emissions of TPP. Copper accumulation is more strongly affected by technogenic depositions and dominated in urban and technogenic zones under the form of oval spots. Konyavska Mountain is the domain of Zn revealing an altitudinal gradient of distribution. Its accumulation proceeds slowly in topsoil, but still, Zn is the most abundant element in studied soils from the Bobov dol valley. The petrogenetic pattern of geochemical suits still predominated in studied soils wherein the iron has the greatest affinity for studied elements. Soil medium reaction (pH) and organic carbon do not control the processes of distribution and accumulation of Cu, Pb and Zn. The lack of statistical correlation with organic carbon resulted from the siliciclastic nature of soil parent rocks and also reveals the prevailing geogenic origin of studied elements.

Key words: Pedoecology, Trace Elements, Distribution, Geochemical Diversity, Background Values

Introduction

Geochemical assay ensures the knowledge of phenomena governing the trace elements distribution in soils. Different geochemical standards such as the average element content in the main types of rocks in the Earth's crust – the continental crust and lithosphere

(Turekian and Wedepohl, 1961; Vinogradov, 1962; Dobrovolskii, 1983; Yaroschevskii, 1990; Wedepohl, 1995; Rudnick and Gao, 2003) are widely used in this study to overcome a geospatial irregularity in soil elemental composition (Vinogradov, 1957; Dobrovolskii, 1983; Alekseenko and Alekseenko, 2013). The last are reference values reflecting the average content of chemical elements over the globe and are consider for one of the most significant achievements of geochemistry during the 20th century. The average content of the elements is an important geochemical characteristic presenting a background amount of elements. The global values, known as "Clarkes" (Vernadskii, 1954) assists in assessing the degree of dispersion or concentration of trace elements in soils. Of special significance are those coefficients, showing the relative enrichment of a chemical element in studied geochemical systems in comparison to its average content in the Earth’s crust, i.e. concentration coefficients. The Clarke concentration (CC) is one of the first introduced coefficients and represents the ratio of the element content in the studied material and the Clarke value of the same element in the Earth's crust. Nowadays, other coefficients are also used to evaluate the geochemical (re)distribution of trace elements in diverse terrestrial environments (Helz et al., 1983; Muller, 1969).

Along with the average content, the establishment of the most important element assemblages determining the specificity and the nature of the geochemical system has a very important methodological role in soil geochemistry. The criterion of this determinative or typomorphic association is the element concentration coefficient regarding the standard which is genetically related to the studied system, i.e., soil forming (parent) materials. It is well known that the composition of the soil parent materials determines the chemistry, mineral composition, structure and characteristics of soils. For this reason, soil parent materials (rocks and sediments) are considered for the genetic standard in soil study. Often the information on the geochemical composition of parent rocks is either incomplete or missing and impedes the study of the diversity of elements and the contributing processes. This information is especially important today when human activity already became a powerful geochemical factor that appreciably affects the distribution of chemical elements in the geosphere.

Thermoelectric Power Plants, (TPP), utilizing solid fuels are one of the major providers of trace elements in the environment, due to the emission of gases and fine ash particles, which contain a number of elements: C, S, H, K, Ca, Al, Cl, Si, Mg, Zn, Mn, Mo, Rb, Ti, Cu, Co, Cr, Br, Pb, Hg, Sb, Cd (Raikov et al., 1984). These emissions contribute not only to the environment pollution but directly affect human health. Therefore, the knowledge of processes governing the accumulation, solubility and cycling of trace elements is nowadays of global importance.

The present study focuses on the geochemical patterns of soils located in the vicinity of the Bobov dol Thermoelectric Power Plant, Bulgaria. The special attention is paid to the amount and geospatial distribution of Cu, Pb and Zn in order to reveal their geochemical behavior, associations, and origin in soils.

Material and methods

Site description

The studied region represents a valley surrounded by Konyavska Mountain. The valley hosts the Bobov dol Thermoelectric Power Plant, which is the main source of trace elements in the region since the early 70s of the 20th century. In the TPP is utilizing mainly lignite and sub-bituminous coal from Bobov dol, Beli Breg, Staniantsi, Chukurovo and Pernik coalfields (Zdravkov et al., 2012). Due to the high ash content in coal, the TPP annually produces about 900 000 t ash (Donchev et al., 2001). Although the Bobov dol Plant works on a program approved to limit the negative impact on the environment, it has only an ash-capture equipment.

The soil cover is generally uniform with few soil varieties presented: Vertic Luvisols, Albic Luvisols, Endocalcic Cambisols, Chromic Cambisols and Luvisols, Eutric Fluvisols, Umbric Leptosols, Colluvic Regosols (WRB, 2014).

In the Bobov dol valley predominate siliciclastic rocks (conglomerate, sandstone, siltstone, and shale) of Paleogene age, which to the North of the TPP contain sub-bituminous coal layers of the Bobov dol coalfield (Marinova, 1993). The Eastern hillsides of the mountain consist of Paleozoic diorite belonging to the Struma Diorite Formation (Marinova, 1993).

Sampling

Soil sampling procedure is based on an irregular site-specific network designed to cover an area of about 8 km^2 around the Bobov dol TPP (Fig. 1). Eighty-five soil samples were taken to a depth of 30 cm in accordance with Bulgarian State Standard (BSS) ISO 10381-1, 2, 4.

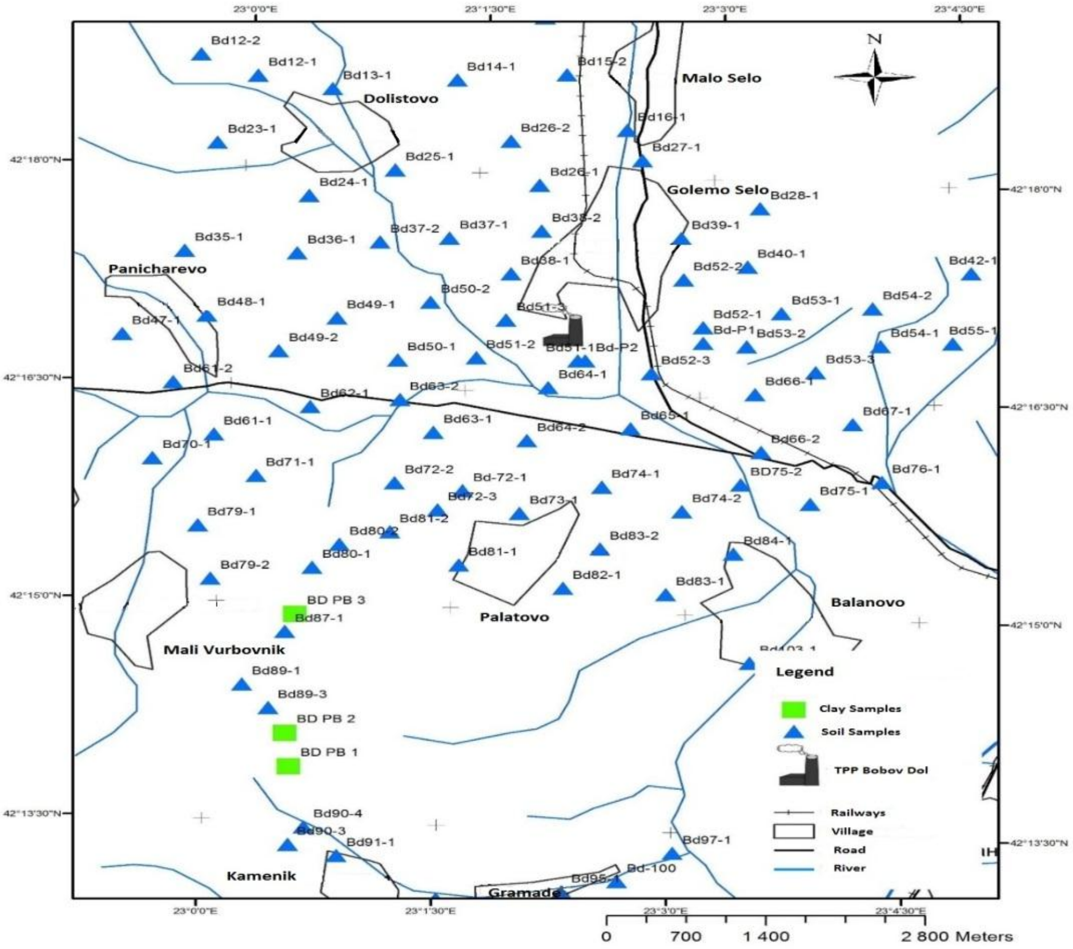

Figure 1. *Location of sampling points*

Three sites disclosed along the conveyor belt transporting the ash to the tailing pond "Kamenik" (Fig. 1) are additionally sampled in order to determine the background content of trace elements in the indigenous soil parent rocks. Although the three rock samples are insufficient to fully characterize the variety of rocks, the results nonetheless present some insights on the concentration of these elements. However, the very similar rock lithology allows us to tentatively accept that the data are sufficiently representative for the studied region. Rock samples were collected from the outcrops by rock hammer and drill to penetrate to 20 cm depth.

Fly ash samples are collected from the intermediate storage tank using surface techniques in duplicate.

Analyses

The content of Cu, Pb, and Zn was determined in all eighty-five samples by the method of soil extraction with aqua regia (ISO 22036:2012). A subset comprising sixty-eight soil samples, representative for all soil varieties has undergone full silicate analysis using lithium metaborate fusion sample preparation as described in the inter-laboratory method CLING BM-2:2013. Soil samples were pre-treated according to ISO 11466:2010 and analyzed in the laboratory of "Geochemistry" (the University of Mining Geology "St. Ivan Rilski", Sofia) by ICP - OES (ICP 720-ES Agilent Technologies). Quality assurance samples (blank and SMR - SOC001-30G) were analyzed every 15 samples. Accuracy and precision for all samples were below 10% and 15% respectively. Determination of pH corresponded to ISO 10390:2010. The modified method of Turin (Kononova, 1963) was applied for organic carbon content analysis.

Table 1. Threshold concentrations (precautionary, maximum permissible and intervention concentrations) of heavy metals in Bulgarian soils

Elements	pH (H_2O)	Precautionary concentrations (A)	Maximum permissible concentrations (B)		Intervention Concentrations (C)
			Arable Lands	Permanent grasslands	
Cu	<6.0	60	80	80	500
	6.0 – 7.4		150	140	
	>7.4		300	200	
Pb	<6.0	45	60	90	500
	6.0 – 7.4		100	130	
	>7.4		120	150	
Zn	<6.0	160	200	220	900
	6.0 – 7.4		300	390	
	>7.4		400	450	

Assessment of trace elements content

The assessment of Cu, Pb, and Zn content is based on the ISRIC methodology applied in SOVEUR's project which uses three degree scale (Van Lynden, 2000): light degree of pollution (L) – concentration of pollutant(s) between A and B values; moderate (M) - concentration of pollutant(s) between B and C values; strong (S) - concentration of pollutant(s) above C. Generally, soils with concentration of pollutant(s) below A value (precautionary concentrations) are unpolluted and considered ―clean". The threshold concentrations (determined in aqua regia as total concentrations, in mg kg^{-1}) adapted to Bulgarian legislation (Regulation 3/2008) are listed in Table 1.

Several concentration coefficients are calculated in order to assess the abundance of Cu, Pb, and Zn in soils: i) the concentration coefficient reflecting the abundance of element in soils compared to the local rocks (local geochemical background) – it is marked with Ccl and is calculated by dividing the average content of each element in studied soils with its average content in local rocks, ii) Ccr reflecting the element abundance compared to its median content (or the average value if the number of samples <100) in main types of Bulgarian rocks (Kuikin et al. 2001) iii) Ccs reflecting the ratio of element content in studied soils and the average element content in Bulgarian soils (Atanasov et al. 2000), and iv) Clarkes (global values estimated for the Earth's crust), coefficient CC (http://www.webelements.com/periodicity/abundance_crust).

In order to provide another approach for evaluation of metal contamination of soils a geoaccumulation index (Muller, 1969) is also calculated (equation 1):

$$I_{geo}= \log_2[Cn/1.5Bn] \quad (1),$$

Where Cn is the measured concentration of the metal n in soils, Bn is the background value for the metal n. The mean of the content of element n in indigenous rocks was accepted as Bn. Igeo values are evaluated by a 7 point scale of Förstner et al. (1993) where: Igeo <0 = practically unpolluted, class 0; 0-1 = unpolluted to moderately polluted, class 1; 1-2 = moderately polluted, class 2; 2-3 = moderately to strongly polluted, class 3; 3-4 = strongly polluted, class 4; 4-5 = strong to very strong pollution, class 5 and > 5 = very strong pollution, class 6.

The range of geochemical background was introduced to reflect the natural variety of content of elements in indigenous rocks and is calculated by traditional formula, equation 2 (Gałuszka et al., 2015):

$$\text{Range of geochemical background} = \text{Mean value} \pm 2 \text{ standard deviations} \quad (2)$$

Geoinformation

Software packages ENVI and ArcGIS are used for the analysis of satellite images ASTER and Digital Elevation Model and mapping. The methodology is described in detail by Ruskov et al. (2012) and involves data obtained by ASTER (Advanced Spaceborne Thermal Emission and Reflection Radiometer) Level 1B scene (ID ASTL1B 0207040929070208060920) calibrated with radiometric and geometric corrections. The image is georeferenced and digital SRTM (shuttle radar topographic mission) model of the relief with a resolution of 90 m is applied for 3D visualization of terrain. The ordinary kriging and spherical model of variogram function are used for data interpolation. The directions of anisotropy are 51 (Cu), 102 (Zn) and 106 (Pb) degrees.

Statistics

Statistical analysis of data was accomplished by Microsoft Excel™ statistical package. Standard error of the mean (SEM) is calculated by the formula of Browne (1979) (equation 3):

$$SEM = \sigma/\sqrt{n} \quad (3)$$

Where, σ is the standard deviation (SD) of the sample; n – sample size.

Results and Discussion

Copper geochemistry

Abundance in litho - and pedosphere. The diversity drivers

The average Cu content in the Earth' crust is 68 mg kg^{-1} (www.webelements.com). In lithosphere, Cu is associated with medium acidic to mafic rocks, although increased copper content is also found in some sedimentary rocks, e.g. shales, sandstones. Further distribution of the element is dominated mainly by anthropogenic factors although the naturally occurring surface copper mineralization or active volcanism also takes place. Among human-induced distribution, the processing of copper ores and coal utilization are of dominant importance. Nriagu and Pacyna (1988) found that the annual man-induced mobilization of Cu into the biosphere can reach 150 thousand tons year^{-1}. According to Yudovich and Ketris (2005) the atmospheric emissions of copper, which mostly due to coal utilization in thermo-electric power plants amount to about 32%.

Distribution of technogenic copper in studied area depends not only on the content and the nature of Cu chemical bond in coal but also on combustion technology. Copper is mainly related to organic matter in coal used in the Bobov dol TPP (Kortenski, 2011) and quantitatively exceeds the Clarke concentration for coal (Table 2). Chukurovo coalfield is remarkable for high Cu content which is about 55-fold higher than Clarke's.

Table 2. *An average content of trace elements in coal utilized in the Bobov Dol TPP (mg kg^{-1})*

Parameter	Beli breg coalfield[1]	Stanyantsi coalfield[1]	Chukurovo coalfield[1]	Pernik coalfield[1]	Bobov dol coalfield[2]	**Average**	**Clarke[3]**
Cu	25,9	7,47	835,0	71,1	50,0	**197,9**	**15,0**
Zn	15,5	36,0	449,0	90,3	133,0	**144,8**	**18,0**
Pb	6,0	21,5	94,2	30,3	15,0	**33,4**	**6,6**

Legend: [1] – Kortenski (2011) data; [2] - Vassilev (1994) data; [3] - Ketris and Yudovich (2009)

Vassilev and Vassileva (1997) investigated the contents of trace elements in the coal and the deposited ash of eleven TPPs in Bulgaria, including Bobov dol TPP, and estimated that between 40 and 60% of the total copper content in coal is emitted into the atmosphere as a aerosol phase. This fact shows the TPP is a driver of the geochemical diversity in the region.

The copper content in studied soils varies in the range from 13.89 up to 53.72 mg kg^{-1} and is higher than 20.03 mg kg^{-1} (the local geochemical background) in 67% of the sampled sites (Table 3).

Regardless of the accumulation trend found in this study copper content is lower that the precautionary level, A (Table 1) revealing the attenuated development of contamination process. The negative mean value of geoaccumulation index (Igeo) also reveals the negligible input of technogenic copper (Table 4).

Table 3. *Basic statistical data on the content of microelements, organic carbon and pH in studied samples from the Bobov dol valley (n = 85, 2 and 3 respectively)*

Parameter	pH	Org. C (%)	Cu	Zn	Pb
			mg kg^{-1}		
Soils					
MIN	4.00	0.43	13.89	21.89	5.68
MAX	7.70	4.41	53.72	102.93	32.82
AVERAGE	5.94	1.29	27.04	57.93	21.96
MEDIAN	5.80	1.23	26.30	56.44	22.91
SD	1.04	0.55	6.99	14.89	5.93
SEM	0.11	0.06	0.76	1.61	0.64
Fly ash from TPP					
AVERAGE	7.7	0.82	32.40	32.21	10.50
Indigenous soil forming rocks					
AVERAGE	Not determined		20.03	46.60	6.07
MEDIAN			22.2	42.2	5.7
SD			5.41	7.68	1.29
Range of geochemical background			9.22 - 30.85	31.24 - 61.96	3.48 - 8.65

Data summarized in Table 4 portray the relative enrichment of the top soil with Cu. The average copper content in studied soils does not significantly diverge from the background content in Bulgarian soils (Ccs), but well displays the element accumulation. The content of Cu in local rocks coincides with a mean reference value for Bulgarian rocks which is an indication of the lack of Cu geochemical anomaly in the Bobov dol valley. Local rocks contained an equal amount of Cu with all types of metamorphites in Bulgaria (Kuikin et al., 2001) and, therefore, Cu content cannot be use as indicative in geologic-petrogenetic context.

Table 4. *Copper average content in different materials (mg kg^{-1}) and accumulation rates in studied soils*

Parameter	Content in studied soils	Local Background value	Ccl	Content in Bulgarian rocks	Ccr	Content in Bulgarian soils	Ccs	Content in the Earth's crust	CC	Igeo
Cu	27.04	20.03	1.35	20.0	1.35	24.0	1.13	68	0.40	-0.10

Legend: Ccl – concentration coefficient of element in studied soils accounting its average content in local rocks as reference value; Ccr – coefficient of concentration showing element abundance in soils compared to its median reference value in Bulgarian rocks; Ccs – element concentration coefficient in studied soils versus its background value (median) in Bulgarian soils; CC – concentration coefficient indicating the degree of element accumulation over the Clarke value; Igeo – index of geoaccumulation

Geospatial distribution and associations in studied soils

The geospatial distribution of copper within the studied area (Fig. 2) is characterized by frequently alternating zone with different element content. Enhanced concentrations of the element are observed in urban sites located on different distance from TPP. These cumulative areas shaped like islands are presumably owing to anthropogenic inputs originated from the domestic use of coal for heating. The technogenic objects as the fly-ash storage tank located close to TPP (next to Bd51-1 in the area of Vertic Luvisols) and the zone for ashes transfer to the tailing pond (points Bd89-1 and 89-3 located on Chomic Cambisol) are also richer in Cu, and reveal the formation of separate Cu-rich areas due to the influence of the TPP activity. Although Cu content in these areas is still lower than the average content in the Earth's crust it is up to 2-fold higher than the local background.

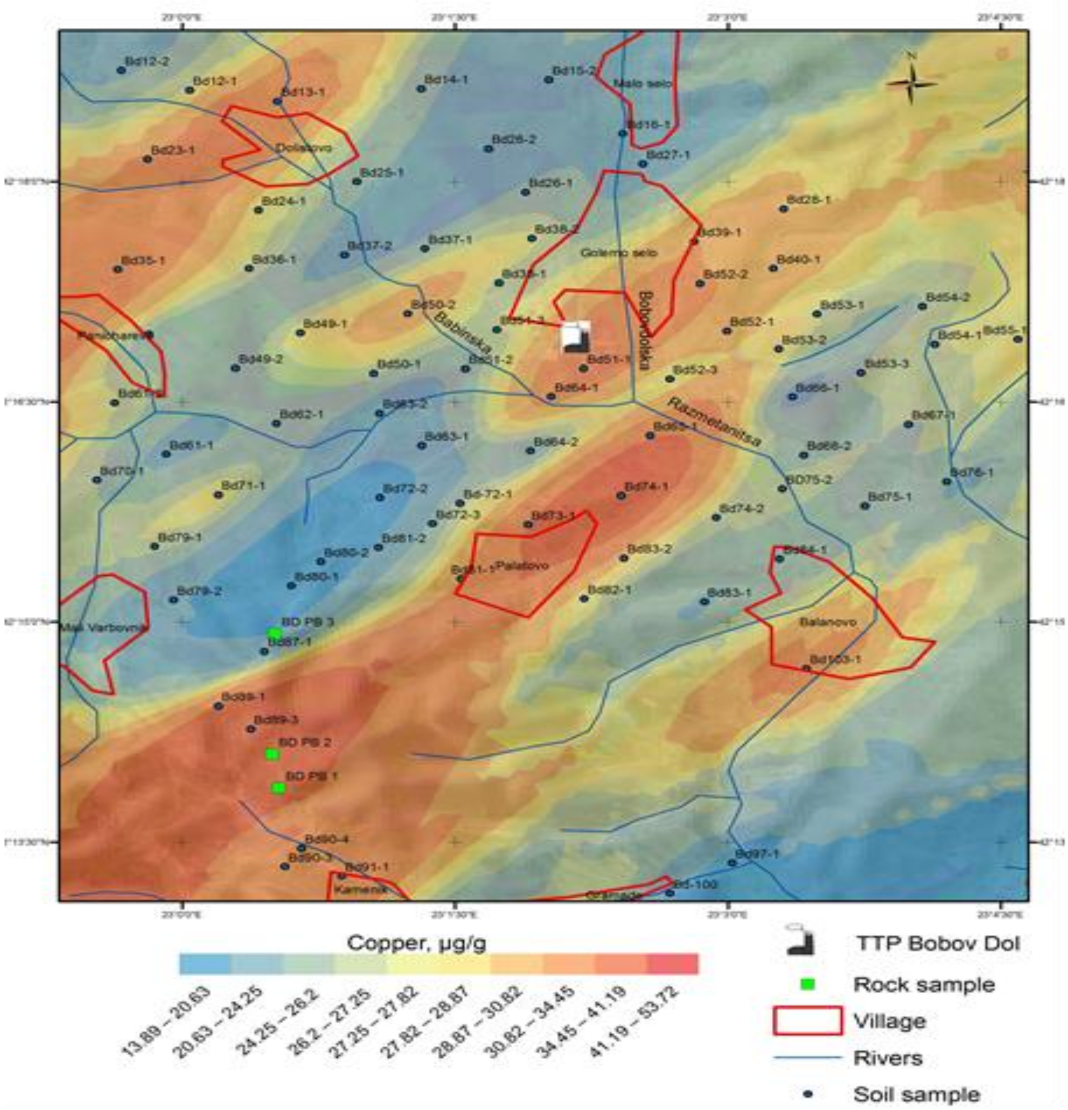

Figure 2. *Geospatial variability of Cu content in the surface layer of studied soils*

Copper distribution seems linked with few elements (Tables 5 and 6; Fig. 3). The content of total copper strongly correlates with the total contents of zinc and iron which are its major alloys in nature and ensure the simultaneous presence of these elements.

Table 5. *Correlation matrix of the content macro- and microelement (n = 68 points sampled)*

Parameter	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SO_3	SiO_2	TiO_2	Cu	Zn	Pb
Al_2O_3	1.00													
CaO	-0.56	1.00												
Fe_2O_3	0.70	-0.24	1.00											
K_2O	0.45	-0.57	0.35	1.00										
MgO	-0.25	0.50	0.05	-0.30	1.00									
MnO	0.25	-0.24	0.39	0.10	-0.13	1.00								
Na_2O	-0.17	-0.23	-0.29	0.28	-0.14	-0.10	1.00							
P_2O_5	0.13	0.22	0.30	0.02	0.18	0.24	0.11	1.00						
SO_3	-0.40	0.80	-0.18	-0.40	-0.01	-0.11	-0.22	0.16	1.00					
SiO_2	0.29	-0.86	-0.06	0.43	-0.70	0.13	0.31	-0.37	-0.57	1.00				
TiO_2	0.64	-0.56	0.58	0.28	-0.29	0.53	-0.01	0.02	-0.35	0.43	1.00			
Cu	0.48	-0.16	0.66	0.21	0.03	0.30	-0.15	0.21	-0.11	-0.04	0.40	1.00		
Zn	0.46	-0.25	0.57	0.39	-0.05	0.37	0.05	0.24	-0.18	0.08	0.49	0.74	1.00	
Pb	0.36	-0.44	0.26	0.33	-0.33	0.40	-0.02	-0.20	-0.32	0.44	0.54	0.38	0.59	1.00

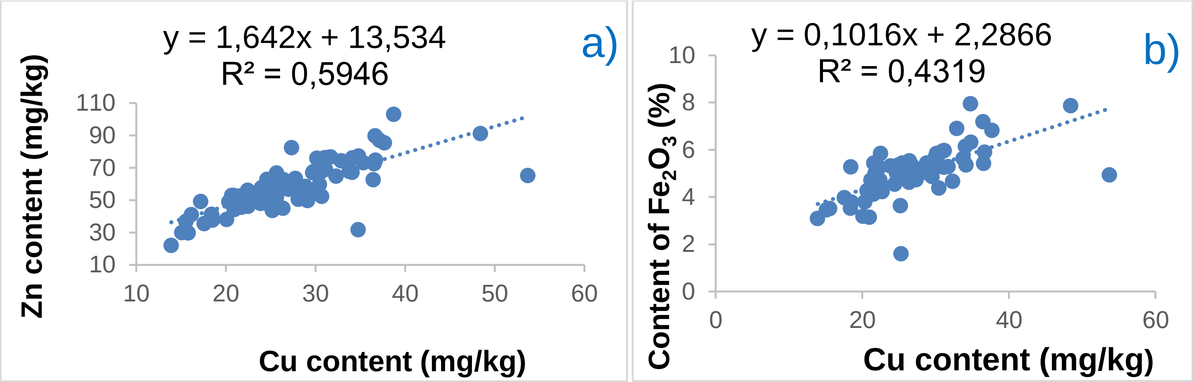

Fig. 3. The correlations between the contents of Cu and Zn (a) and Cu and total Fe (b)

The metal well correlated with iron extractable with aqua regia (Table 6) and hence discovers another analytical way to study Cu association in soils.

Table 6. Correlation matrix of the content of microelement and diversity drivers (n = 85)

Parameter	Cu	Zn	Pb	Fe	pH	Corg
Cu	1.00					
Zn	0.77	1.00				
Pb	0.37	0.45	1.00			
Fe	0.74	0.79	0.50	1.00		
pH	0.20	0.15	-0.36	-0.02	1.00	
Corg	-0.01	-0.02	-0.26	-0.12	0.19	1.00

The weaker correlation with Al suggests that the metal occurs in a non-diffuse form which is the most stable form of this metal in soils (Kabata-Pendias, 2000). The element occurs predominantly in the form of mineral compounds as revealed by the lack of correlation with organic carbon. Having in mind that siliciclastic rocks spread in the region are formed by inorganic processes the lack of correlation with organic carbon is not surprising. Moreover, it also accentuates the prevailing petrogenetic origin of Cu in studied soils. No statistical correlation was found between the content of total copper and pH (Table 6), which can be explained by the weak dependence of Cu geochemistry on pH. Baker and Senft (1995), Adriano (1986) and Kabata-Pendias (2000) suggest that the adsorption and mobility of copper (and lead) in uncontaminated soil is less dependent on pH, which partly explains Cu accumulation in studied soils.

Zinc geochemistry

Abundance in litho- and pedosphere. The diversity drivers

The average zinc content in rocks of the Earth's crust is 79 mg kg^{-1}. Increased concentrations are found in basic igneous rocks (100 mg kg^{-1}) and argillaceous sedimentary rocks (120-200 mg kg^{-1}, Alloway, 2008).

In unpolluted soils, the total zinc content is largely dependent upon the geochemical composition of the parent rock materials and fluctuates between 10-300 mg kg^{-1} at an average of 50 mg kg^{-1} (Kiekens, 1995). Zinc accumulates in soils as a result of both natural and anthropogenic processes, but the latter has a greater share. Many studies reported on pollution of soils located near the plants of metallurgical industry or ameliorated with fertilizers containing zinc (Kabata-Pendias and Mookherjee, 2007; Alloway, 2008). Nicholson et al. (2003) announced that Zn is the most cumulative element among all trace elements monitored in soils which accumulation rate could reach 217 g/ha year^{-1}.

Emissions from coal burning can influence lithogenic background of Zn in studied area (Table 2). Compared to the elements such as As, Co, Pb, which are highly volatile and almost completely pass into gaseous form, the formation of zinc gaseous phase is a complex process and depends on more factors - the combustion temperature, the excess of oxygen, and Zn chemical form (Yudovich and Ketris, 2005). For these reasons, the amount of emitted zinc varies considerably (Yudovich and Ketris, 2005) and can result in variable levels of zinc dressed soils (Alloway, 2008).

The content of zinc in studied soil surface layers widely varies from 21.89 to 102.93 mg kg^{-1} and in 79% of the analyzed samples exceeds the average content in the local bedrocks. However, compared with the soil background and precautionary values in Bulgaria studied soils are poorer in zinc (Tables 1, 3, 7).

Table 7. *Zinc average content in different materials (mg kg^{-1}) and accumulation rates in studied soils*

Parameter	Content in studied soils	Local Background value	Ccl	Content in Bulgarian rocks	Ccr	Content in Bulgarian soils	Ccs	Content in the Earth's crust	CC	Igeo
Zn	57.93	46.6	1.24	45.0	1.29	69.0	0.97	79	0.73	-0.05

High values of SD (Table 3) compromise to some extent the homogeneity of results but zinc accumulation in studied soils is still demonstrated (Table 7). Zinc is another element that tends to accumulate in studied soils but the degree of accumulation still slightly exceeds the background values according to the data in Table 7.

Geospatial distribution and associations in studied soils

Zones of zinc accumulation are located on hillsides of the Konyavska Mountain while the plane part of the area is occupied by sedimentary materials with low zinc content (Fig. 4).

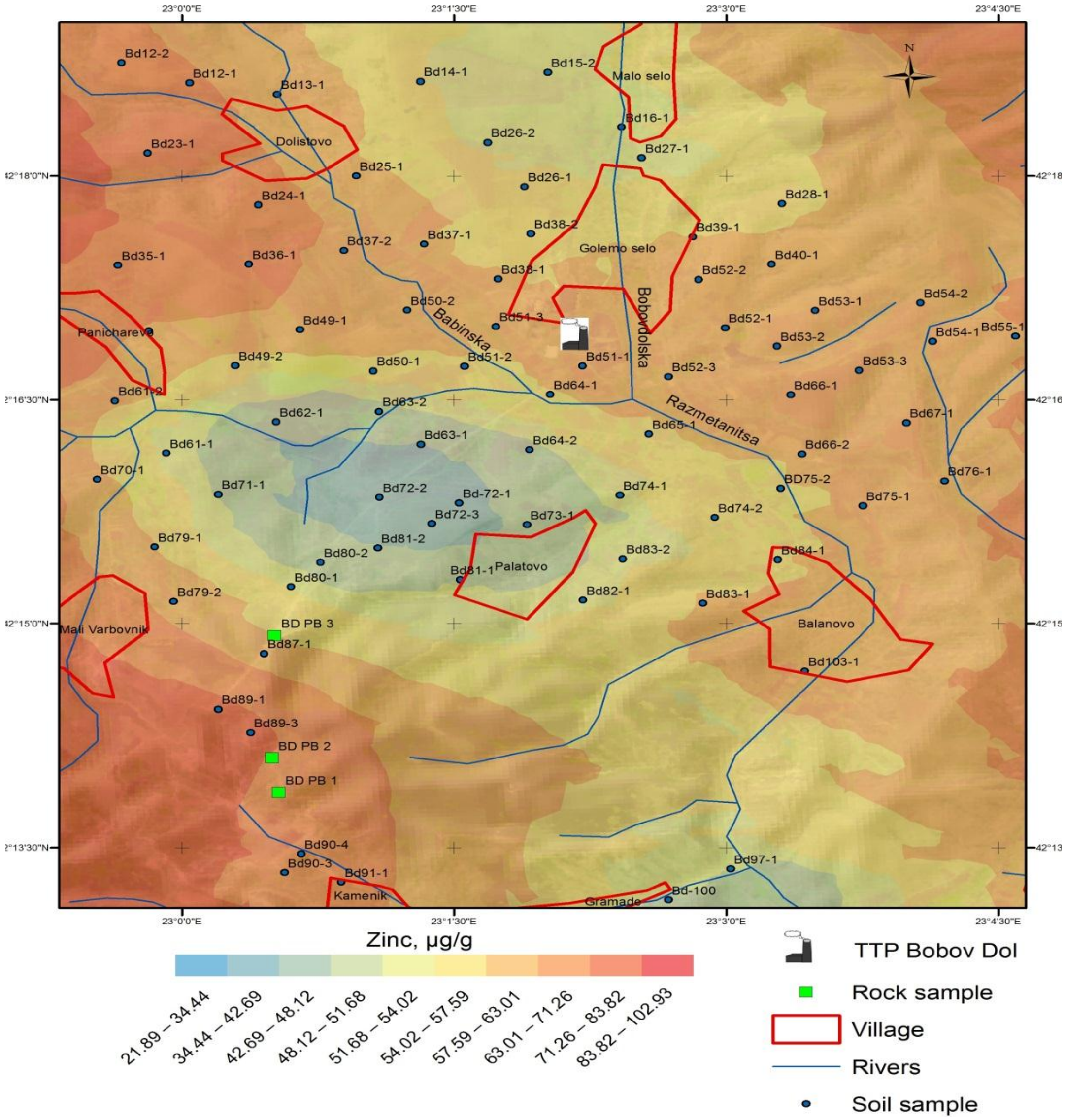

Figure 4. Geospatial variability of Zn content in the surface layer of studied soils

The area of Bobov dol TPP characterized with Zn content higher than the average but soils (Chomic Cambisol) surrounded the transfer facilities for ash (Bd89-1 and 89-3) are the most enriched. This shows again that TPP is a modern driver of geochemical diversity in the region.

Zinc also occurs in inorganic form - the correlation coefficient with organic carbon is negligible (Table 6). It linkage with Fe (Fig. 5), including iron extracted by aqua regia (Fig. 5b) seems stable and franklinite ($ZnFe_2O_4$), which contains both Fe^{3+} and Fe^{2+} (Lindsay, 1972), could be the mineral controlling the mobility of zinc in studied soils irrespectively of the other adsorption mechanisms.

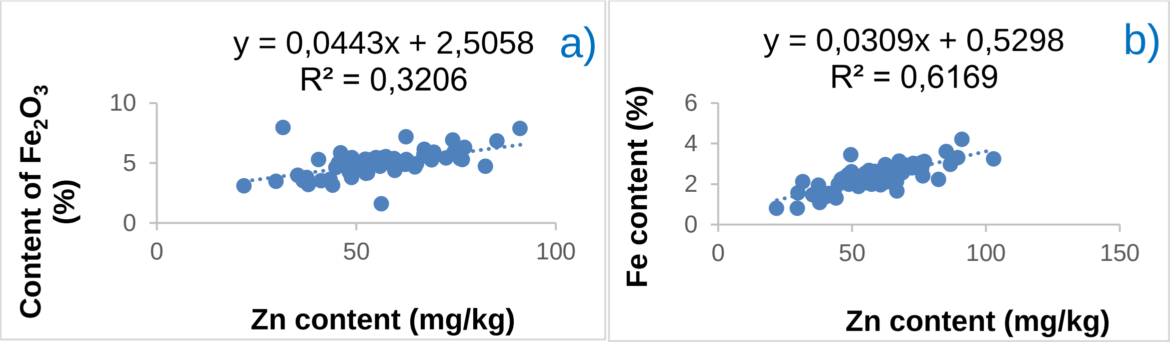

Figure 5. *The correlations between the contents of Zn and total Fe (a) and Zn and AR-extractable Fe (b)*

The association of Zn and Cu, which is the only one between trace metals is also a hallmark of studied pedogeochemical system (Fig. 3a). No correlation was found between the content of zinc and pH (Table 6), which could be regarded as a complex result of the specific sorption of the element (Orlov, 1995; Alloway, 2008) and low content of organic matter.

Lead geochemistry

Abundance in litho- and pedosphere. The diversity drivers

Lead content in the Earth's crust is not high (10 mg kg^{-1}, Table 8). The metal usually is prone to concentrate in acidic and moderately acidic igneous rocks (Kuikin et al., 2001; Kabata-Pendias and Mookherjee, 2007). In fact, regardless of the concentration, it occurs in almost all types of rocks (Aubert and Pinta, 1977).

Many processes in pedosphere immobilize Pb and retain it in soils and sediments (Davies, 1995; Pais and Benton, 1997; Kabata-Pendias, 2000), although the prime source of Pb in soils is parent rocks. Soil lead content widely varies and in some European soils reaches 970 mg kg^{-1} at an average of 32.6 mg kg^{-1} (Salminen et al., 2005). Kabata-Pendias (2000) reckoned 25 mg kg^{-1} for baseline concentration in top soil on the global scale.

Nowadays, lead accumulation in soils is irreversible process contributing to unparalleled perturbations of its biogeochemical cycle (Davies, 1995; Nriagu, 1990). The most significant anthropogenic sources of lead are metallurgical enterprises and thermal power plants utilizing fossil fuel (Pacyna, 1987; Kabata-Pendias and Mookherjee, 2007). The lead content in the TPP's emission depends on the element content in coal, and on its chemical form (Xu et al., 2003; Yudovich and Ketris, 2005). The average concentration of an element in coal, the Clarke, is usually low - 6,6 mg kg^{-1} in lignite and brown coal and 9 mg kg^{-1} in black and anthracite (Ketris and Yudovich, 2009). Among coal that is utilized in the Bobov dol TPP predominated ones with lead content exceeding Clarke's (Table 2).

3.3.2. Geospatial distribution and associations in studied soils

Lead content ranges from 5.68 to 32.82 mg kg^{-1} (Table 3) in studied soils and in 77% of sampled sites exceeds 18 mg kg^{-1}, i.e., the background (average) content of the element in Bulgarian unpolluted soils (Table 8).

Table 8. *Lead average content in different materials (mg kg^{-1}) and accumulation rates in studied soils*

Para-meter	Content in studied soils	Local Back-ground value	Ccl	Content in Bulgarian rocks	Ccr	Content in Bulgarian soils	Ccs	Content in the Earth's crust	CC	Igeo
Pb	21.96	6.07	3.62	21.0	1.05	18.0	1.22	10	2.20	0.39

This range indicates the lack of pollution according to ISRIC methodology but an assessment based on geoaccumulation index reveals the initial stage of contamination – Igeo class 1. Very high level of Pb accumulation is displayed by Ccl coefficient showing the enrichment rate of soils compared to background concentration in parent rocks.

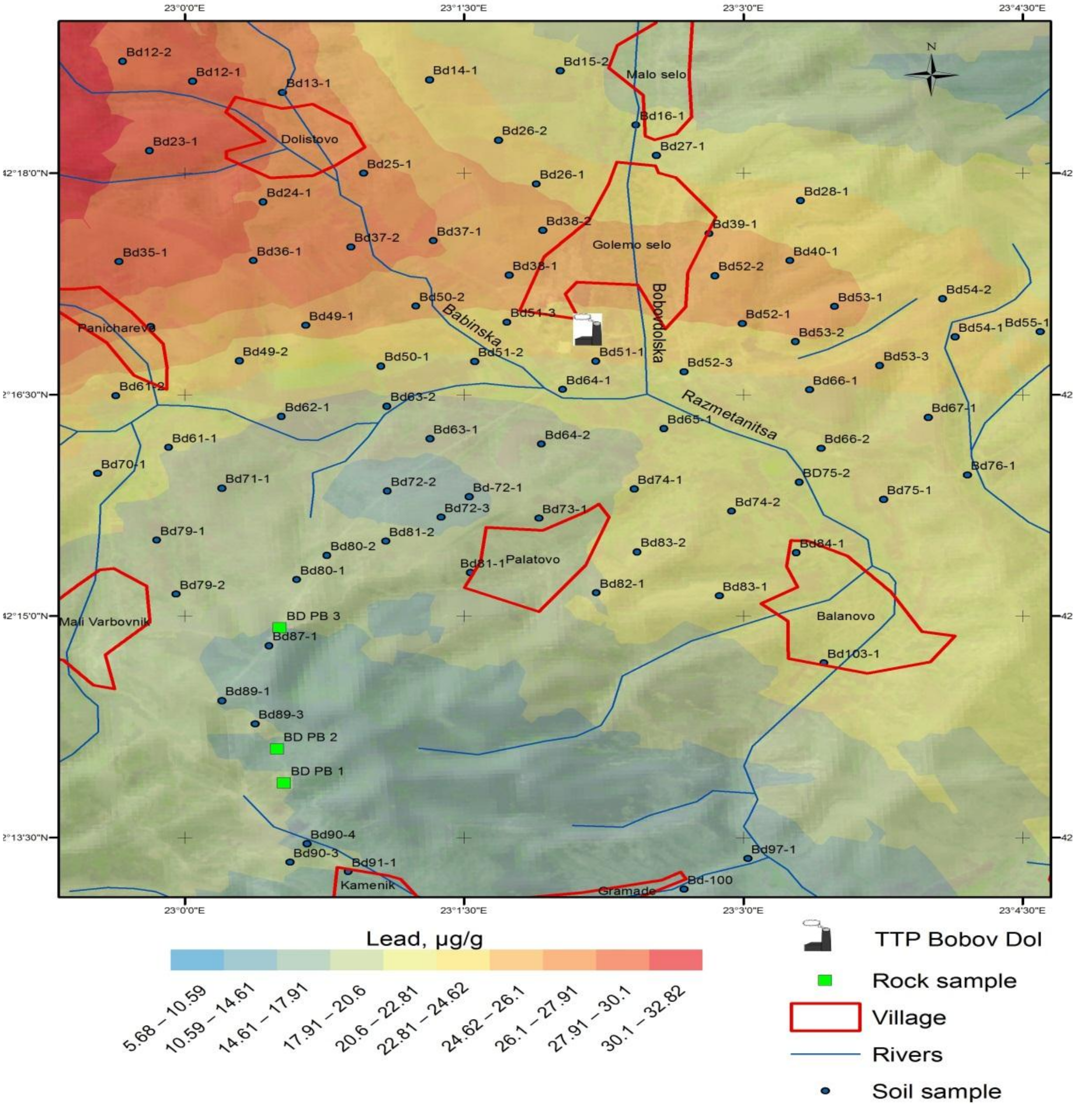

Figure 6. *Geospatial variability of Pb content in the surface layer of studied soils*

The higher content of Pb in soils located in various coal regions of Bulgaria established in previous studies validates the lower baseline level of the element in studied soils (Tsolova et al., 2014). Therefore, local geochemical hallmarks of rocks could better reflect the abundance of lead in studied region.

In geospatial aspect lead content decreased after the Razmetanitsa catchment and along the technogenic "corridor" for ash transport is close to the average value in studied soils. The highest concentrations are established northwest of Bobov dol TPP on the hillsides of the Konyavska Mountain (Fig. 6) where Chromic Luvisols prevailed. Besides the lithogenic nature, these concentrations may have a modern origin that could be assigned to human-induced redistribution of elements within the research area and beyond as well.

The lack of significant correlations with studied microelements is the reason to assume that Pb is distributed with other geologic suits in the Bobov dol valley. The calculated correlations between the content of lead and major elements give an indication of the prevalence of its inorganic forms, mainly associated with titanium, AR-extracted iron, silicon and negatively with calcium oxide (Tables 5, 6).

Obviously, Pb’s affinity for Fe is stronger than the interactions with base metals such as Cu (r = 0.37) and Zn (r = 0.45). Dominant distribution of the mineral lead is confirmed by the lack of correlation with organic carbon. There is also no correlation accounted between the lead amount and pH (Table 6).

It should be noted that the aqua regia is maybe not the most appropriate reagent for analysis of technogenic lead originated in coal combustion. Czaplicka and Buzek (2011) while studied the dust emitted from Non-Ferrous Metallurgy Processes, found that the element presents mainly in two chemical forms: as salts, soluble in an alkaline solution or as compounds that produce plumbites (Na_2PbO_2) in reaction with sodium hydroxide.

Conclusions

The indigenous soil parent rocks create a negative geochemical anomaly with a lower content of studied elements compared to Clarkes (element content in the Earth’s crust). In surface horizons of studied soils – different varieties of Luvisols, Cambisols, Fluvisols, Leptosols and Regosols the accumulation of Cu, Pb and Zn is verified by concentration coefficients accounting the element average contents in soil forming rocks.

Lead quickly accumulates in soils and becomes the only element with a positive index of geoaccumulation. It weakly associates with most of the studied elements but occurs allied to iron compounds extractable with aqua regia. Lead, therefore, tends to follow a separate mode of geospatial distribution which is influenced by geogenic factors and the aerosol emissions of TPP as well.

Copper accumulation is also evidenced by geochemical hallmarks included in the study. It, however, is more strongly affected by technogenic receipts and dominated in urban and technogenic zones under the form of oval spots. Konyavska Mountain is the domain of Zn revealing an altitudinal gradient of distribution. Its accumulation proceeds slowly in topsoil, but Zn is still the most abundant element in studied soils from the Bobov dol valley.

The litho-petrogenetic pattern of geochemical assemblages still predominated in studied soils wherein iron manifests the greatest affinity for studied elements. Soil medium reaction (pH) and organic carbon do not distinctly control the distribution and accumulation of Cu, Pb, and Zn. The lack of statistical correlation with organic carbon resulted from the siliciclastic nature of soil parent rocks and also reveals the prevailing geogenic origin of studied elements.

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Content and Behavior of Radiocesium in Undisturbed Bulgarian Soils

Ivanka Yordanova, Donka Staneva, Lidia Misheva

N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection
1331 Sofia, 7 Shosse Bankya str.
Corresponding Author: Ivanka Yordanova, e-mail: ivanka.yordanova@gmail.com

Abstract

Results of the radiological monitoring of radiocesium content in soils from different regions of the country are presented and discussed in this work. Plain, hilly and mountain areas covering two thirds of the country are included in the study. The samples are analyzed by gamma-spectrometry. Some aspects of the fixation of Cesium in the soil are studied. Laboratory experiments were carried out trying to explain the quick distribution of Cs down the soil profile in 1986, immediately after the Chernobyl's contamination. It was established that the mobility of Cesium in soil is higher in the initial period after deposition and decreases with time.

Key words: Soil, Radioactivity, Gamma-Spectrometry

Introduction

The radioecological studies of earth's crust and especially soil are very important part of radioecology as they give basic data for estimation and prediction of radionuclide content in agricultural production and thus in food and man. Nuclear accidents, such as the Chernobyl accident, have released large amounts of radionuclides into the environment. The accident in Chernobyl nuclear power plant (ChNPP) caused the largest uncontrolled radioactive release into the environment dispersed on over the entire northern hemisphere It was estimated that about 85 PBq of ^{137}Cs were released in the accident (UNSCEAR, 2000). The radionuclides with long half-life like ^{137}Cs deposited after the accident remain in the environment, mainly in the soil, for decades and are relevant for the environmental monitoring. Analysis of radionuclide content of soil, plants, water and knowledge of the behavior of the radionuclides in soil–plant system provides an important part of a data basis for dose estimation (UNSCEAR, 1993 and UNSCEAR, 2000).

Bulgaria was among the European countries with relatively high contamination as a result of Chernobyl accident. The activity concentrations of man-made radionuclides in the Bulgarian soils increased considerably.(Tsvetkov, et al 2006.). Subject of the studies were undisturbed soils from high mountain areas, hills and plains (the region of Kozloduy NPP and the Danube river valley).(Staneva, et al., 2012; Yordanova, et al.2006; Staneva, et al., 2006). The areas around Kozloduy NPP are of special interest. Such data can be used as a baseline from which we can detect future release of radioactive nuclides.

The mobility of radiocesium in the soil is one of the most important factors controlling its long-term transfer to man via terrestrial pathways. That is why the knowledge about the behavior of this radionuclide in the soil is of significant importance, as the insufficient understanding of the fundamental processes taking place in the soil compartment causes large uncertainties on the environmental forecast.

Up till now, 30 years later, ^{137}Cs is still detected in all soil samples and represent a potential danger for the contamination of the plant production through the root feeding. Our work aims assessment of local background values for ^{137}Cs in soil on the base of regular radiological monitoring of virgin soils from high mountain areas, hills and plains covering most of the territory of Bulgaria.

Material and Methods

For the purposes of the radiation monitoring of the soils in our country sampling of undisturbed soils is done annually from one and the same sampling sites covering almost the whole area of the country. Sampling areas are specified considering the wind direction and difference in altitude so-that different soil types are included. According to the altitude of the investigated areas three groups have been defined: plains – mainly North Bulgaria, (around the NPP Kosloduy and along the river Danube – 40 sampling points *[sp]*); semi-mountainous (the Sofia plain – 10 sp, and the valleys of Struma and Mesta rivers (15 sp)) and mountains area - in South Bulgaria (the Rodopa mountain– 25 sp).(Yordanova I., et al.2014; Yordanova I., et al.2015)

The soil samples were taken according to the procedure defined in Bulgarian Governmental Standard BGS17.4.5.01-85 for soil sampling from permanent sites annually from one and the same sampling points from the soil layer 0-5 cm were collected. At some sites the samples are collected from up to 40 cm depth in layers of 5 cm.

The soil samples are homogenized, dried at 80ºC and sieved through a 2-mm mesh before measurement with a gamma-spectrometer. A Canberra high-purity germanium detector with 20% efficiency an energy resolution of 1.8 keV for ^{60}Co γ-ray energy line at 1332 keV was used. The measuring system included a multichannel analyzer DSA 1000(Canberra, USA). The spectrum was analyzed by GENIE-2000 software with measurement uncertainties less 10%. Typical counting times were 19–24 h. The ^{137}Cs concentrations in soil were obtained by measuring the activity at 661.62 keV.

For the laboratory experiments we have used – *Fluvisols* soil, widespread in our country. This soil was part of a long-term vegetation pot experiment for studying the uptake of cesium by plants from contaminated with radiocesium (^{134}Cs) soil. (Ts. Bineva et al. 2012; D. Staneva et al, 2009)

The soil was additionally contaminated with ^{137}Cs in chloride form. Desorption of Cs was done with a lactate-acetate buffer, used for determination of exchangeable forms of K^+ in the soil (Radov A. C., et al. 1985). Soil aliquots (2g) were suspended in desorption solutions and shaken. After centrifugation the supernatant was removed and analyzed for ^{137}Cs using gamma spectrometry.Different time periods and solid: liquid phase ratios were tested in order to find optimal conditions for desorption and determination of different Cs fixation-sites

Results and Discussion

Until 1986 the mean values for the specific activities of ^{137}Cs were as follows: Northern Bulgaria - 10 Bq.kg^{-1} and Sothern Bulgaria - 26 Bq.kg^{-1} (Najdenov M., 1986, Najdenov M., Staneva D., 1987). These values were received by calculating the arithmetic mean from the results for specific activities in surface soil samples for each area observed.. The mean square deviation at this averaging was up to 40%.

After the Chernobyl disaster in 1986 the radio-ecological status of the soils in Bulgaria concerning the men-made radioactivity has changed radically because of the massive deposition of radioactive elements

Results for Ceasium-137 activities in soils are presented on figures 1..

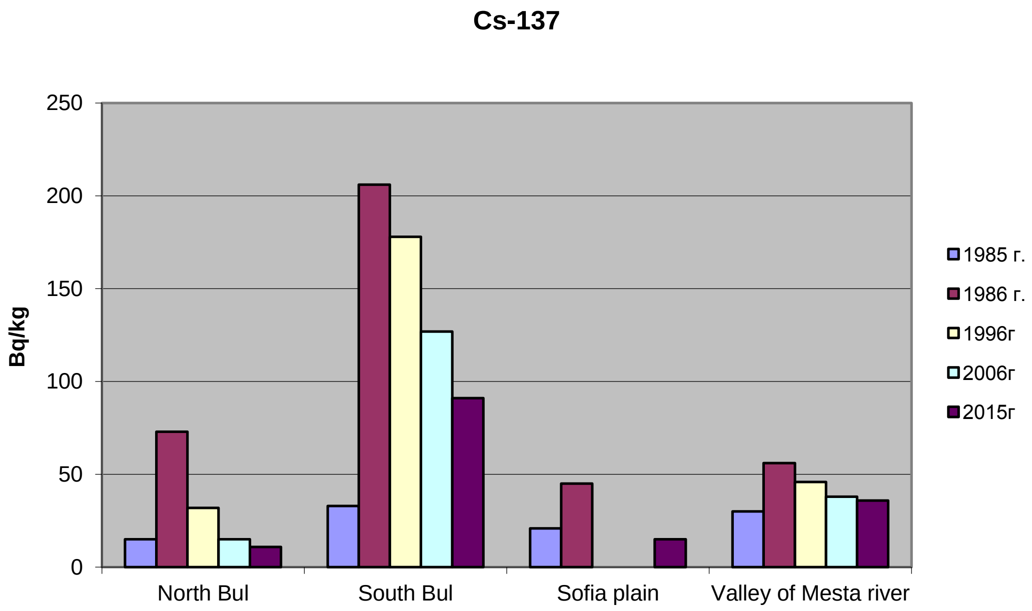

Fig. 1. *Average values for ^{137}Cs content in soils [Bq.kg^{-1} dry wt]*

It is to be noted that the surface pollution is very non- homogeneous and this brings about great variations in calculating the arithmetic mean values. For Ceasium-137 the variations are between 30% and 60% for the different areas. This is the reason why it is difficult to make categorical evaluations of an obvious increase or reduction of the contents of these radio-nuclides in the upper soil layers. The most probable reason for this non-homogeneity is the type of deposition in May 1986 after the Chernobyl's accident. It was wet deposition for a short time combined with heavy rainfall.

The specific activities of ^{137}Cs are four - five times higher in the soils from Southern Bulgaria than in those from Northern part. For SB the mean values vary in the years between 160 and 280 Bq.kg^{-1} , while for NB – between 40 and 60 Bq.kg^{-1}.This can be explained with the difference in altitude and what is more the radioactive cloud in 1986 passed twice the Southern part of the country and there the quantity of the rainfall was higher.(Yordanova I., et al. 2007)

We can compare these results with data from neighbouring country like Greece (Vosniakos F.K., et al. 2000) They publish results for mean concentration of ^{137}Cs in soils for the period 1986-1990 (44.3 ± 28.6 Bq.kg^{-1}). This difference in the level of contamination is caused by the difference in meteorological conditions, type of deposition and difference in altitude.

After 1996 the researches on status and dynamics of the radio-active pollutions of the soils in the country was directed mainly towards an expansion of the sites number for the purpose of encompassing a greater territory, whereby regions have been researched on, which have potentially been exposed to radio-active pollutions, as for instance the high mountainous soils of the Rila and Pirin mountains.Figure 2 shows the results obtained from the analyses of soils in Northern Bulgaria, the plain area (around the Nuclear Power Station Kosloduy and along the river Danube); areas along the rivers Struma and Mesta, and the region of the Rila and Pirin mountains.As becomes obvious, the contents of radioceasium in the soils of Northern Bulgaria and the valleys of the rivers Struma and Mesta are comparable while for the mountains soil (Rila and Pirin), relatively higher values for this radio-nuclide have been observed, which is natural due to the geographic situation.

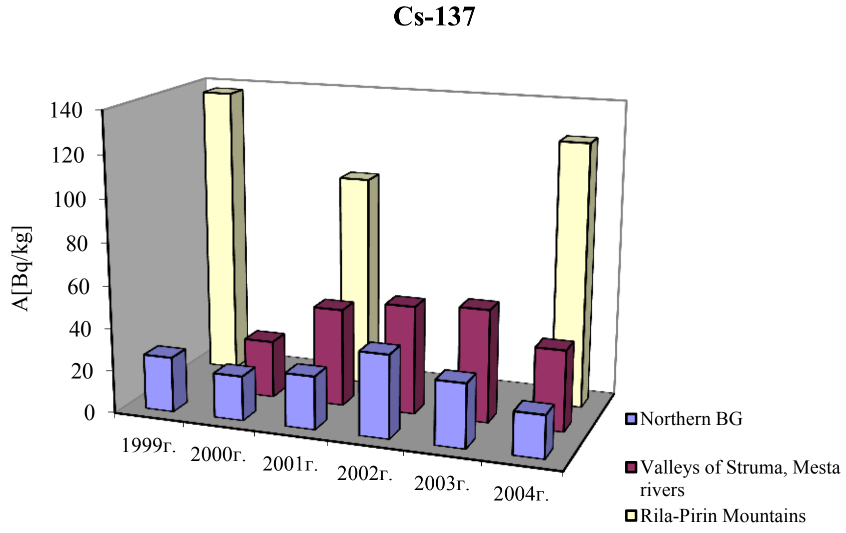

Fig.2. *Average values of Cs-137 content in soils [Bq.kg^{-1} dry wt] for the period of 1999–2004*

The results presented in fig.1 show that except for South Bulgaria (the Rhodope Mountains) the amount of ^{137}Cs in the surface soil layer of 0-5 cm for 2015 is comparable to that before the accident in Chernobyl's NPP,. This decrease is mainly due to the natural decay of cesium 137 and to a very small degree to migration processes in depth of the soil profile.

During the first months after the accident in 1986 we established that Chernobyl's Caesium indicated by ^{134}Cs had migrated down to a depth of 30 cm .(Tsvetkov Ts., et al 2006.), a fact reported by other authors too (Wolfgang S. and Kurt B., 1996). Fig. 3 shows the distribution in depth of Cs in three different soil types -*Luvic phaeozem, Phaeozem, Fluvisols (FAO classification*)

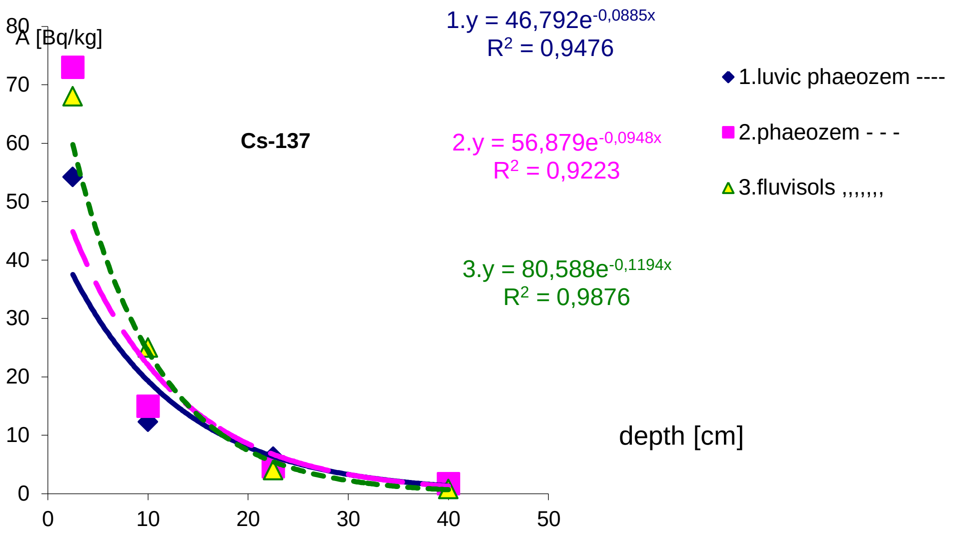

Fig. 3. *Distribution of ^{137}Cs in depth down the soil profile*

Our observation in the years following the Chernobyl accident did not show significant changes in this distribution of Cs down the soil profile and intensive migration (*Tsvetkov Ts., et al 2006*). For this reason we performed our laboratory experiment to study the behavior in soil of “old” and newly incorporated cesium. ^{134}Cs – as part of the long-term vegetation pot experiment was in the soil for more than ten years. ^{137}Cs was applied additionally and after twenty days desorption was carried out.

Based on the fact that Caesium and Potassium are analogues as chemical elements, we applied lactate-acetate buffer used to determine the exchange forms of Potassium. The ratio between solid and liquid phase was 1: 25, which is accepted in the methodology for defining the exchangable forms of Potassium (Radov A. C., et al. 1985). In this case our purpose was to study in more details the degree of fixation of a newly introduced Caesium or Caesium, which has stayed in the soil for years, for which we used *Fluvisols*. The results are presented in table 1.

Table 1. *Percentage of activity desorbed with lactate-acetate buffer*

.	**1 hour shaking**	**2 hour shaking**	**3 hour shaking**	**4 hour shaking**	**5 hour shaking**	**6 hour shaking**
^{137}Cs	40%	40%	50%	40%	50%	54%
^{134}Cs	4,6%	5,4%	4,5%	4,5%	3,1%	3,7%

With this experiment a considerable difference in behavior between a newly introduced (newcomer) and an “old” Caesium is displayed. In both cases at the end of the second hour a dynamic balance was established, where the degree of desorption did not change.Notwithstanding the established strong fixation of Caesium in the soil with time the plants grown on soil contaminated with ^{134}Cs absorb the element and with the years no considerable reduction of the transfer coefficients was to be observed (Bineva Tz., et al. 2005; Staneva D., et al. 2004).

Conclusion

As a conclusion we may say that:

The levels of ^{137}Cs established in the surface soil layer of 0-5 cm for 2015 are comparable to those detected before the accident in Chernobyl's NPP for North Bulgaria and the plain and hilly areas of South Bulgaria. This decrease is mainly due to the natural decay of ^{137}Cs;

In the region of Rodopa mountains in South Bulgaria the levels of ^{137}Cs are still relatively higher as the deposition of radionuclides in 1986 was more intensive on these areas.

The amount of radiocesium in the soil from the studied areas combined with the established immobilization of Cs with time are such that do not require additional initiatives for radiation protection.

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Method for Evaluation of Soil Conditions Suitable for Growing Emmer and Einkorn Wheat

Zornitsa Mitreva, Veneta Krasteva,Veselin Pankov

N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection

1331 Sofia, 7 Shosse Bankya str.
Corresponding Author: Zornitsa Mitreva, e-mail: zuza_na@abv.bg

Abstract

Method is developed for the field rating of main soil characteristics that define the suitability for growing emmer and einkorn wheat. Soil texture of the fallow land, depth of the humus horizon, depth of the soil profile, texture differentiation of the soil profile, soil reaction, humus content and groundwater level have been evaluated. The method is harmonized with the officially accepted in Bulgaria parametric methods of the system of field ratings and the categorization of the agricultural lands. The end result is an evaluation of the soil conditions and a soil rating.

Key words: Field Ratings, Soil, Soil Characteristics, Emmer and Einkorn Wheat

Introduction

The emmer and einkorn are a type of wheat and some of the oldest food sources of humanity. Einkorn is thought to have originated in the upper area of the fertile crescent of the Near East (Tigris-Euphrates regions). Cultivated einkorn is Triticum monococcum (Stallknecht et al., 1996). Triticum dicoccum or emmer wheat rapidly spread to all farming areas in the Near East during the seventh millennium BC and became the most important cereal (Feldman, 1976). In Bulgaria they are grown on a quite limited area mostly on soils with low fertility not suitable for other types of wheat, in mountainous regions and near some river valleys. They have lower yield than bread wheat Triticum aestivum (Longin et al., 2016).

Nevertheless, during the last few years there is a growing interest towards the biological agriculture and healthy nutrition, these types of wheat are very beneficial. For example emmer wheat has high total antioxidant activity, total phenolics, ferulic acid and flavonoids whereas einkorn is rich in lutein (Serpen et al., 2008). Moreover, the emmer and einkorn wheat have fewer requirements in terms of soil and climatic conditions, rarely suffer from plant diseases, and overall fewer pesticides are needed (Koedzhikov et al, 1977). These qualities are a good ground for research in the field that will be useful and applicable in practice.

The aim of our research is the creation of scales for evaluation of the main soil characteristics in accordance with the environmental requirements of the einkorn and emmer wheat. Additional goal is to evaluate the soil conditions and create a soil rating using parametric methods.

Material and Methods

Biological requirements of the crops

These “ancient” wheat types i.e. emmer wheat and einkorn wheat are major products of organic agriculture owing to the increased interest in the search of unconventional food sources with low initial investments.

The characteristics of emmer wheat T. dicoccum Schranc are the following: Its ears are flattened with different thickness and in each of them there are two grains which give its name. The grains are small and flattened. Mainly spring types are known from this wheat type.

The einkorn wheat T. monococcum L has tender, small ears, compact and completely flattened. In every ear there is only one grain. The einkorn wheat is also represented by spring types. An interesting feature is that the grains are covered with color paleas which protect it from diseases and infestation from pests which is a property of its genome. Owing to the fact that they are exceptionally valuable crops, growing them can be environmentally friendly, as well (Koedzhikov et al., 1977). These wheat types are a suitable alternative to the farmers in Bulgaria because they can include one more crop in their crop rotation plan. This would guarantee them stable income in conditions of sudden climate change.

Soil conditions and the requirements of the crops

The crops are very unpretentious to the soil conditions. They can be grown on poor, impermeable, stony soils with low fertility. For optimal development and yield the most suitable soil has high clay content (content of physical clay 45-60%), with deep (over 40 cm) and rich in organic carbon content (over 2%) humus accumulative horizon, neutral to weakly basic soil reaction (pH in H2O 6,5 - 7,5), low level of the groundwater (100-200 cm under the soil surface), friable structure and good physical and aquatic characteristics. The soil has to provide high intensity root nutrition and water supply. For that reason the most suitable soils are the chernozems (leached, typical and calcareous), smolnitsas and leached cinnamonic forest soils.

Suitable predecessors are crops that leave the soil clean from weeds and in good structural conditions. Planting is not recommended following other cereals, i.e. wheat, barley, oats, triticale. The crops are unpretentious in their nutritional requirements and fertilization is not recommended (Koedzhikov et al., 1977)

Parametric method comparable to “Methods for work on the agricultural land cadaster in Bulgaria”, 1988, (Petrov et al., 1988) is applied. The idea is to use new method for evaluation of additional crops that are missing at present.

Results and Discussion

The soil characteristics that are taken into account are the following:

1. Soil texture of the fallow land presented using the content of the physical clay, sum of particles < 0.01 mm (%); depth of the humus horizon (cm);
2. Depth of the soil profile (cm). The characteristic is evaluated only on shallow soils, developed on hard rock with the depth of the hard rock till 50 cm (root area).

3. Texture differentiation of the profile described using the texture coefficient. The ratio of the amount of the clay content (per cent amount of the sum of the particles with size <0.001 mm) in B horizon to the amount in A horizon.
4. Soil reaction (pH in H_2O).
5. Organic content – humus (%).
6. Groundwater level (cm). The soil texture is also included in the evaluation of this characteristic (Georgiev, 2007; Krasteva, 2002; Mitreva, 2008). Using this characteristic the following characteristics are taken into account: the influence of the capillary rise of the groundwater, the conditions of marshiness, overmoisture or beneficial use of the groundwater.

Seven rating scales are developed, for individual rating of each one of the enumerated characteristics. (Rating scales with consecutive numbers 1 to 7) are presented below in Tables 1-7.

Table 1. *Evaluation (Btx) of the soil texture in fallow land (Tx)*

Tx (sum of particles < 0.01mm %)			Btx (ratings*)
	<=	5	0
5	÷	10	10
10	÷	20	30
20	÷	30	70
30	÷	45	90
45	÷	60	100
	>	60	70
* At the end the values are multiplied by 2			

Table 2. *Evaluation (Bthh) of the depth of the soil humus horizon (Thh)*

Thh (cm)	Bthh (ratings)
1 - 20	40
20 - 40	80
> 40	100

Table 3. Evaluation (Btsp) of the depth of the soil profile (Ttsp)

Tsp (cm)	Btsp (ratings*)
<= 30	10
30 ÷ 50	30
> 50	Not evaluated
* Only for soils developed on hard rock. At the end the values are multiplied by 3.	

Table 4. Evaluation (Btc) of the texture difference coefficient (Tc)

Tc (texture coefficient)	Btc (ratings)
<=1	80
1 – 1.3	100
1.3 - 2	90
>2	50

Table 5. Evaluation (Bph) of the soil reaction (pH in H_2O)

pH (in H_2O)			Bph (ratings)
	<=	5.0	60
5.0	÷	7.5	100
	>	7.5	80

Table 6. Evaluation (Bhc) of the humus content (Hc)

Hc (%)	Bhc (ratings)
< =1.0	50
1.0 – 2.0	80
>2.0	100

Table 7. Evaluation (Bgwt) of groundwater level (Gwt) relative to soil texture.

↓ Gwt (cm) Bgwt (rating)↘	Range Tx (%)				
	< =20	20 ÷ 45	45÷60	>60	
< = 50	50	30	10	0	
50 ÷ 100	90	70	40	20	
100 ÷ 200	100	100	100	80	

In the presented scales for individual rating of soil characteristics the principles of the officially accepted methods are applied (Petrov et al., 1988). Because of the similarities of the requirements of the crops the scales are created for both of them. When groundwater rating is not evaluated because it is below 200 cm and therefore is not a limiting factor it is calculated in the equations with a rating of 100. The ratings are in a range of 0 to 100 rating grades. The optimal values of the characteristics receive a maximum grade; the restrictive values receive a lower grade. When the conditions are extremely unsuitable the grade becomes zero. When one of the grades is zero the entire soil rating equals zero. In shallow soils developed on hard rock the rating task is solved using Equation (1). In deep soils the rating task is solved using Equation (2).

$$SR = \frac{2Btx + Bthh + 3Btsp + Btc + Bph + Bhc + Bgwt}{10} \tag{1}$$

$$SR = \frac{2Btx + Bthh + Btc + Bph + Bhc + Bgwt}{7} \tag{2}$$

Where

SR – soil rating

Btx – Rating for the soil texture.

Bthh – Rating for the depth of the humus horizon.

Btsp – Rating for the depth of the soil profile.

Btc – Rating for the texture differentiation of the soil.

Bph – Rating for soil reaction (pH in H_2O).

Bhc – Rating for organic content represented by humus content (%).

Bgwt – Rating for groundwater level.

The soil ratings alone cannot be used to measure the suitability of the land for growing emmer and einkorn wheat because other factors also influence the development and yield of the crop exemplified by erosion and accumulation, salinization, stoniness, climate, etc.. Taking into consideration the influence of these characteristics leads to field ratings of the whole land which can be performed by further research.

To demonstrate the methods in Table 8 are evaluated three soil examples.

Table 8. Examples of application of the methodology

Soil code	*Indexes and values of the characteristics and ratings*							
	Tx (%)	*Thh (cm)*	*Tsp (cm)*	*Tc*	*Ph*	*Hc (%)*	*Gwt (cm)*	
KCR	*34*	*50*	*90*	*0.9*	*6.8*	*2.1*	*Deep*	
	Btx	Bthh	Btsp	Btc	Bph	Bhc	Bgwt	SR
	90*2	100	Not evaluated	80	100	100	100	94
Soil code	*Indexes and values of the characteristics and ratings*							
	Tx (%)	*Thh (cm)*	*Tsp (cm)*	*Tc*	*Ph*	*Hc (%)*	*Gwt (cm)*	
ALM	*48*	*30*	*100*	*1.3*	*4.8*	*1.7*	*120*	
	Btx	Bthh	Btsp	Btc	Bph	Bhc	Bgwt	SR
	100*2	80	Not evaluated	100	60	80	100	89
Soil code	*Indexes and values of the characteristics and ratings*							
	Tx (%)	*Thh (cm)*	*Tsp (cm)*	*Tc*	*Ph*	*Hc (%)*	*Gwt (cm)*	
KI	*19*	*20*	*20*	*0,9*	*5,5*	*1,3*	*deep*	
	Btx	Bthh	Btsp	Btc	Bph	Bhc	Bgwt	SR
	30*2	40	10*3	80	100	80	100	49

Legeng:
KCR – Calcareous chernozems, average depth.
ALM – Alluvial meadow soils, deep.
KI – Cinnamonic forest soils, shallow, low and middle eroded.
SR – Soil rating.
All indexes are from tables with consecutive numbers from 1 to 7

The calcareous chernozems with average depth receive the highest rating.

Conclusion

A method for evaluation of the main soil characteristics in accordance with the emmer wheat and einkorn wheat requirements is suggested. The method is harmonized with the officially accepted in Bulgaria parametric methods that comprise the system of field ratings and categorization of the agricultural lands. The end result is a rating of the soil characteristics, i.e. soil rating. Further algorithms for erosion or accumulation of the soil, stoniness, salinity level and climate can be added in further research to reach a full field rating and then the method developed can be used for evaluating the land suitable for growing emmer and einkorn wheat.

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Maize (Zea mays) Biomass and Yield as Influenced by Leguminous and Non-Leguminous Mulch Types in Southwestern Nigeria

Matthew Awopegba*, Moses Awodun, Segun Oladele*****

**, **Department of Crop, Soil and Pest Management, Federal University of Technology, P. M. B 704 Akure. Nigeria*
****Department of Agronomy, Adekunle Ajasin University Akungba Akoko, Nigeria*
Corresponding Author: Segun Oladele e-mail: segun.oladele@aaua.edu.ng

Abstract

Two field experiments were conducted at the Teaching and Research Farm of the Federal University of Technology Akure (7^0 17'N, 15^0 14'E) in the rainforest zone of southwestern Nigeria during the dry and wet seasons of 2013 and 2014 to evaluate the comparative effects of leguminous and non-leguminous mulch types on the growth and yield of maize (*Zea mays* L.). The leguminous plant mulch was *Cajanus cajan* while the non-legume mulch type was *Chromolaena odorata* applied at the rate of 5 t ha^{-1} and NPK 20:10:10 fertilizer was applied at the rate of 200 kg ha^{-1}. The treatment was laid out in randomized complete block design (RCBD) with three replicates. The growth and yield parameters in maize and changes in soil chemical properties were monitored and determined in both experiments. Significant increases in soil organic carbon (SOC), available P, total N, exchangeable bases, maize biomass and yield parameters over the control were obtained for the *Cajanus cajan* mulch treatment applied at 5 t ha^{-1} which were similar to the NPK fertilizer treatment. However, NPK treatment produced the highest grain yields in the dry season while *Cajanus cajan* and NPK treatments produced the highest biomass and grain yields in the wet season.

Keywords: Legumes, non-legumes, mulch, maize, biomass, yield, soil health

Introduction

The physical condition of a soil is one of the fundamental factors affecting crop growth, development and yield. This is because the soil physical properties have very high degree of correlation with crop production and have high influence on soil fertility and crop performance (Nnaji, 2009). However, with the removal of vegetation and subsequently cropping, fertility maintenance becomes a serious problem. The indicators are rapid decline of organic matter and soil nutrients, high soil acidity and erosion which culminate in sharp decline in crop yields. The numerous soil problems are further compounded by the seasonality and erratic distribution of rainfall which results in varying periods of dry spells separated by wet periods (Enwezor *et al.,* 1979). There is, therefore, the need to develop farm management practices that would conserve moisture in the soil to tide crops over during periods of dry spells and protect the soil against erosion during erosive storms. Studies carried out in Nigeria and elsewhere have shown that mulches not only conserved soil moisture and prevented erosion, they also increased soil fauna and flora activities, suppressed weeds and maintained high crop yields (Kurshid *et al.,* 2006; Anikwe *et al.,* 2007; Seyfi and Rashidi, 2007; Essien *et al*., 2009). Different types of materials such as wheat straw, rice straw or husk, plastic film, grass, wood, sand and oil layer have been used as mulches (Khurshid *et al.,* 2006; Seyfi and Rashidi, 2007). Legumes are very important both ecologically and agriculturally because they are responsible for a substantial part of the global flux of N_2 from atmospheric N_2 to fixed form (Patriarca *et al.,* 2002). Also, the low fertility status of most tropical soils hinders maize production as maize has a strong nutrient exhausting effect on the soil. It was observed that maize failed to produce well-filled cobs in plots without adequate nutrients (Adediran and Banjoko, 2003). Mulching with residues of weeds such as siam weed and Mexican sunflower was found to increase yields of crops such as maize (Ojeniyi and Adetoro, 1993; Falade and Ojeniyi, 1997; Awodun and Ojeniyi, 1999) and soil nutrient contents. The mulches have fertilizer effect also (Taiwo and Makinde, 2005). Pigeon peas (*Cajanus cajan*) have been used effectively as a cover crop in coffee, corn, and other crops. Benefits of the pigeon pea cover crop included improved soil fertility, weed competition, and increased arthropod diversity (Odeny, 2007). The roots of pigeon pea excrete organic acids such as citric, piscidic, and tartaric acid, which help to mobilize P in the soil. The leaves that fall from pigeon pea before harvest provide a mulch and can add as much as 90 kg N/ha to the soil that then mineralizes relatively slowly during the subsequent season, releasing N for the next maize crop (Adu-Gyamfi *et al.,* 2007). It was reported that, mulches from pigeon pea residues can be effective for weed suppression (Ekeleme *et al.,* 2003). The use of pigeon peas in multiple cropping systems resulted in greater resource use efficiency, increased crop productivity, more stable or resilient systems over time and less economic risks to small farmers in the tropics (Waddington *et al.,* 2007). It was reported by Chikowo *et al., (*2004) that, pigeon pea develops effective mycorrhizal associations, improving nutrient uptake efficiency, also Shibata and Yano (2003) reported that mycorrhizal associations enhanced the ability of pigeon peas to absorb P ten times faster compared to one time uptake without root inoculation. It was found out that, Siam weed (*Chromolaena odorata*) is widespread throughout the humid forest zone of West Africa and it grows luxuriantly and rejuvenates the soil. Its effectiveness in yam mulching had been reported (Akanbi and Ojeniyi, 2007). Farmers observed that fields colonized by C. *odorata* produced better yields of maize and groundnut. It is, however, obvious that with its abundant biomass production, C. *odorata* contributes significantly to the buildup of organic matter and leads to an increase of the soil pH on very acid soils. *Chromolaena odorata* may enhance the regeneration in heavily disturbed forests that are dominated by grasses. This is due to the improved soil conditions that enhance secondary succession as a result of the presence of this weed. If combined with appropriate tree species, C. *odorata* may be more useful. *Chromolaena odorata* shoot contains 1.26% N, 0.67% P, 1.08% potassium (K), 2.33% Calcium and 0.005% Mg (Olabode *et al*., 2007). *Moringa oleifera* has been reported to improve crop yield by improving soil fertility and providing semi-shade, useful in intercropping systems where intense direct sunlight can damage crops. Also, reducing fallow periods with sown leguminous plants such as *Calopogonium mucunoides* was found to be a technically feasible, low-input method of improving soil nutrient levels for rice cropping in the Guinea and Sudan savannah regions of northern Ghana (Yiridoe *et al.*, 2006) Thus, the objective of this study was to evaluate the comparative effect of leguminous and non-leguminous mulch types on growth and yield component of maize.

Material and Methods

The experiments were conducted at the Teaching and Research Farm of the Federal University of Technology Akure, Ondo State, Nigeria. The area lies within the tropical rainforest belt (7^0 17'N, 15^0 14'E). The rainfall pattern of Akure is bimodal with a wet season of about eight months occurring between April and October and with a brief dry spell which in most cases occur in the second half of August. The peak rainfall periods are June/July and September/October while the short dry season lasts from November to March. The mean daily temperature ranges from 27^0C to 37^0C. The experimental field was mechanically cleared, ploughed and harrowed. The Soil at the experimental site is a clay loam alfisol classified as clayey skeletal oxic-paleustaif, four core samples were collected at random from each treatment plot with the aid of a soil auger at a depth of (0-15cm). The collected core samples were homogenized and a total of twelve composite soil samples were collected from the trial sites for determination of chemical properties before planting and after harvest. The samples were air dried at room temperature, crushed and sieved through a 2mm mesh and subjected to particle size analysis using the Bouyoucos (1951) method. The soil pH was determined by using 1:2 of 10 g of soil to 20 ml distilled water ratio suspension. The suspension was stirred for 30 minutes and determined by glass electrodes pH meters which were standardized with a buffer of pH 7. Total nitrogen in the soil was analysed using Kjeldahl method, while available phosphorus was extracted using Olsen's extract and the P in the extract was determined via the use of spectrophotometer. The organic matter was determined using Walkley-Black (1934) wet Oxidation method. Potassium (K^+), Calcium (Ca^{2+}), Sodium (Na^+), and Magnesium (Mg^{2+}) were extracted by 1M Ammonium acetate (NH_4OAC), at pH 7 and the extracts were determined on a flame photometer while Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) were determined by ethylene di-amine tetra acetic acid (EDTA) titration (AOAC, 1997). The site was sectioned out into blocks and plots. Improved hybrid seeds of maize (*Zea mays* L.) was collected from Ondo State Agricultural Development Project Seed Centre in Akure were sown in an already prepared experimental field manually at 3 cm depth. Maize was sown at a spacing of 60 x 30 cm (55,555 plants/ha) with the total number of twenty-eight (28) maize plants per plot. Weed control was done manually by hand pulling and hoeing. The experiments was laid out in a randomized complete block design (RCBD) and lasted for three months with the treatment in three (3) replicates. Each replicate consisted of three (3) treatments. Total land area measured 207 m^2 (23m x 9m) with 9 plots in all and each plot size measured $4m^2$ with 1 m alley ways between plots and replicates. The first experiment was conducted between 2nd of September to 30th November, 2013 while the second experiment was conducted between 1st of May to 30th of July, 2014. Chopped leafy vegetative parts of both leguminous and non-leguminous mulch was applied at 5 t ha^{-1} as treatments across the blocks and plots while NPK 20:10:10 at a recommended rate of 200 kg ha^{-1}. Plant height was measured with a metre rule and number of leaves by direct counting of the leaves. Leaf area was measured with leaf area metre. Dry matter yield was determined using the formulae: Dry matter yield (kg ha^{-1}) = kg stover yield m^{-2} x $10{,}000m^2$. Shelling percentage, grain yield, biomass yield and harvest index were determined by using standard procedures. The data obtained on the morphological characteristics, yield and yield components were analyzed statistically using the Analysis of Variance. Data were analyzed using SPSS statistical package and the treatment means comparison done with the Duncan's Multiple Range Test (DMRT).

Results and Discussion

Table 1 shows the chemical and physical properties. The pH of the soil was 6.18 and the values of OC, OM, N, P and K in the soil were 1.98 g kg^{-1}, 3.42 g kg^{-1}, 0.48 g kg^{-1}, 3.78 mg kg^{-1} and 0.60 cmol kg^{-1} respectively. The other exchangeable bases such as Na, Ca and Mg were 0.49 cmol kg^{-1}, 2.10 cmol kg^{-1} and 1.50 cmol kg^{-1} respectively. Soil particle fraction showed that the soils are sandy clay loam in texture indicating that the soil is low in organic matter content and high in percentage of sand. The soil was characterized by slight acid with pH value of 6.18. The fertility of the soil was low compared with established critical levels. The organic matter content was a bit high, however the soil was deficient in N and P while K component of the soil was high. The Mg was high while calcium was low. Table 2 shows the effect of leguminous and non-leguminous mulch treatment on soil chemical properties. *Cajanus cajan* mulch treatment applied at 5t/ha improved soil properties by increasing SOC, available P, total N and exchangeable bases after maize harvest while *C.odorata* significantly increased soil pH over other treatments. This increase observed in the *C.odorata* treatment might be due to the effects of the chopped mulch which improved soil potassium and magnesium thereby reducing acidity. Similar results were observed by Egbe et al., 2012 who reported increase in soil pH from *Callandra, Gliricidia* and *Senna* prunnings applied on an andosol in cameroon. Ojeniyi *et al.* (2012) also reported that Mexican sunflower and siam weed respectively reduced soil bulk density, increased total porosity and soil water content. It also increased the soil nutrient levels and subsequently produced high growth of maize. Fallow lands under C. *odorata* produce higher yields of crops such as maize and cassava. This is probably due to the recycling of nutrients and higher litter fall which improves organic matter and soil structure (Torres and Palier, 1989).Table 3 shows the macro-mineral composition of the leguminous and non-leguminous mulch type used in this study. *Cajanus cajan* had the highest content of N (12.44%) of the two mulch materials due to its nitrogen fixing and storage ability while NPK fertilizer had higher N content (18.25%). P content of *Cajanus cajan* (9.86%) was also higher than *Chromolaena odorata* (1.70%) mulch and NPK fertilizer (9.65%), K content (4.12%) was lower than that of NPK fertilizer (9.74%), however it was higher when compared with *Chromolaena odorata* (1.12%). *Chromolaena odorata* had the highest calcium content of the mulch types (3.96mg/kg) and NPK fertilizer (1.87mg/kg). *Cajanus cajan* had the highest composition of Mg (2.90mg/kg) amongst the mulch types while NPK fertilizer recorded the lowest Mg composition (1.21mg/kg). Figures 1 and 2 show the effects of leguminous, non-leguminous mulches and NPK fertilizer on number of leaves per maize plant at two weeks intervals over a period of 9 weeks after treatment application in 2013 and 2014, respectively. In both years, there were no significant differences in the numbers of leaves of maize at 3WAP. Significantly, *Chromolaena odorata* mulch treatment at 5 t ha^{-1} and NPK at 200 kg ha^{-1} had the highest number of leaves in both years. In both years all shrub treatments and NPK fertilizer significantly increased the number of leaves produced when compared with the control at 5, 7 and 9 weeks after treatment application. No significant differences were indicated between *Chromolaena odorata* treatment and NPK fertilizer, but there were variations in the number of leaves in their response to treatments. It was also observed in both years that the number of leaves reduced in 11WAP as a result of shedding of leaves. Significant increases in plant height over the control were obtained for all the treatments throughout the period of growth of maize (Figures 3 and 4). However, NPK fertilizer consistently produced plants with the tallest height while control had the shortest plants in this study. In both years, all the mulches and NPK fertilizer significantly increased maize leaf area throughout the evaluation period when compared with the control (Figure 5 and 6). A comparison of the *Cajanus cajan* mulch treatment and NPK resulted in significantly greater leaf area in the second year. However, NPK at manifested the highest leaf area throughout the evaluation period. Leguminous mulching significantly promoted vegetative growth over the non-leguminous mulch, this may be ascribed to a better soil microclimatic modulation potentials of mulching practice. Steady moisture content and well textured soil probably lead to unrestricted root growth and development which enabled subsequent increase in nutrient absorption. This study corroborated the report of Ba, (1992) who observed that non-mulched plot yielded cucumber with low plant height, branches number, flowers and fruits. Chung, (1987) and Aliudin (1986) also reported that mulches conserved more soil moisture, enhanced vegetative growth and yield contributing characters of garlic. Grass-mulched soil maintained high moisture content to a depth of 60cm and Hatfield et al. (2001) reported a 34-50% reduction in soil water evaporation (Adeoye, 1984), crop residues (grasses, lantana leaves, sorghum, cotton and maize stubbles) as mulches reduces moisture losses and irrigation requirement. There were significant differences in dry matter yields among the treatments in both years. A comparison of the treatments indicated that shrub mulch and NPK fertilizer resulted in significantly greater dry matter yields than the control; NPK gave significantly highest dry matter. The control had significantly lowest dry matter yields in both years (Tables 4 and 5). Significant differences in grain yields were found among the treatments in both years (Tables 4 and 5). Analysis identified two general grouping of the treatments; NPK fertilizer gave the significantly highest grain yield in both years (Tables 4 and 5), except in 2014 when NPK and *Cajanus cajan* had similar yields. The trend in biomass yield as affected by treatments is similar in both years (Tables 4 and 5). The NPK fertilizer significantly increased biomass yield over the mulch treatments and control. The NPK standard gave the significantly highest biomass yield while control gave the lowest yield. Dygima and Demkouma (1986) reported black polyethylene mulch on eggplant and tomato yielding 3.3 times and 2.3 times respectively higher when compared with no mulch since it creates good environment for crops (Thakur et al., 2000). Significant increases in the shelling percentage were noted for the *Chromolaena odorata* mulch treatment and NPK standard over the *Cajanus cajan* and control in both years. However, *Chromolaena odorata* and NPK were not significantly different from *Cajanus cajan* treatment in 2013 (Tables 4 and 5). Significant differences in harvest index were found due to treatment effects in both years (Tables 4 and 5). NPK standard resulted in significantly greater harvest index than the *Cajanus cajan, Chromolaena odorata* mulch treatments and control in the first year while there were no significant differences among NPK, *Cajanus cajan, Chromolaena odorata* mulch treatments in the second year. Control had the lowest harvest index in the second year. The results of this study is corroborated by Muhammad et al. (2009) and Anikwe (2000) who all stated that use of mulch materials either leguminous or non-leguminous as used in this research creates a sound micro ecological environment of the soil, thereby increasing soil moisture content, reducing water infiltration rates, reduces soil sealing, wind and water erosion, weed complexities and the decomposed chopped mulch improves soil aggregation, fertility which leads to a cumulative increase in dry matter and crop yield.

Table 1: *Physico-chemical properties of experimental soil at a depth of (0-15cm) before planting*

Properties	**Values**
Physical composition (g kg^{-1})	
Sand	52.57
Silt	18.99
Clay	28.44
Textural class	Sandy clay loam
Chemical characteristics	
pH in H_2O (1:1)	6.18
Organic carbon (g kg^{-1})	1.98
Organic matter (g kg^{-1})	3.42
Available P (mg kg^{-1})	3.78
Total N (g kg^{-1})	0.48
Exchangeable bases (cmol kg^{-1})	
Ca	2.10
Mg	1.50
K	0.60
Na	0.49

Table 2: *Physico-chemical properties of top soil (0 –15 cm) of experimental field after harvesting of maize*

Treatments	**pH(H_20)**	**OC (g/kg)**	**P (mg/kg)**	**N (g/kg)**	**Ca**	**Mg**	**K**	**Na**
					(cmol/kg)			
NPK (20:10:10)	6.12ab	1.74d	3.21b	0.56b	2.50b	1.40b	0.72c	0.24c
Cajanus cajan	5.74b	2.10a	5.23a	0.88a	3.10a	1.90a	0.86b	0.32b
C. odorata	6.62a	1.96bc	3.92ab	0.62b	2.20bcd	1.20bc	0.60d	0.29bc
Control	6.12ab	1.68d	2.12c	0.48bc	2.10bcd	1.40b	0.97b	0.35b

*Means followed by the same letter within each column are not significantly different (P=0.05) as indicated by Duncan's Multiple Range Test.

Table 3: *Chemical composition of shrub mulch and 20:10:10 NPK fertilizer*

Elements	**NPK**	***Cajanus cajan***	***Chromolaena odorata***
N (%)	18.25	12.44	4.22
P (%)	9.65	9.86	1.70
K (%)	9.74	4.12	1.12
Ca (mg/kg)	1.87	3.82	3.96
Mg (mg/kg)	1.21	2.90	1.60

*n = 4

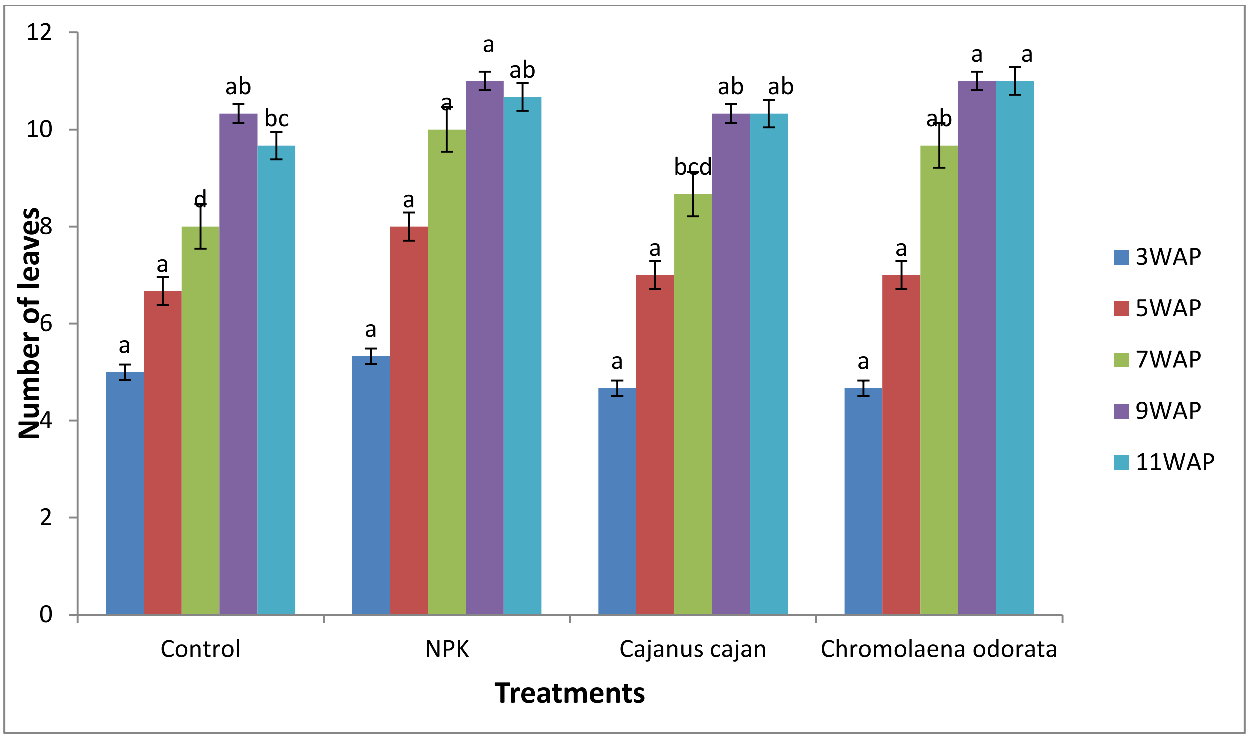

Figure 1: *The effects of mulches and NPK on the number of leaves at different stages of growth of maize in 2013*

Legend: *WAP: Weeks after planting*

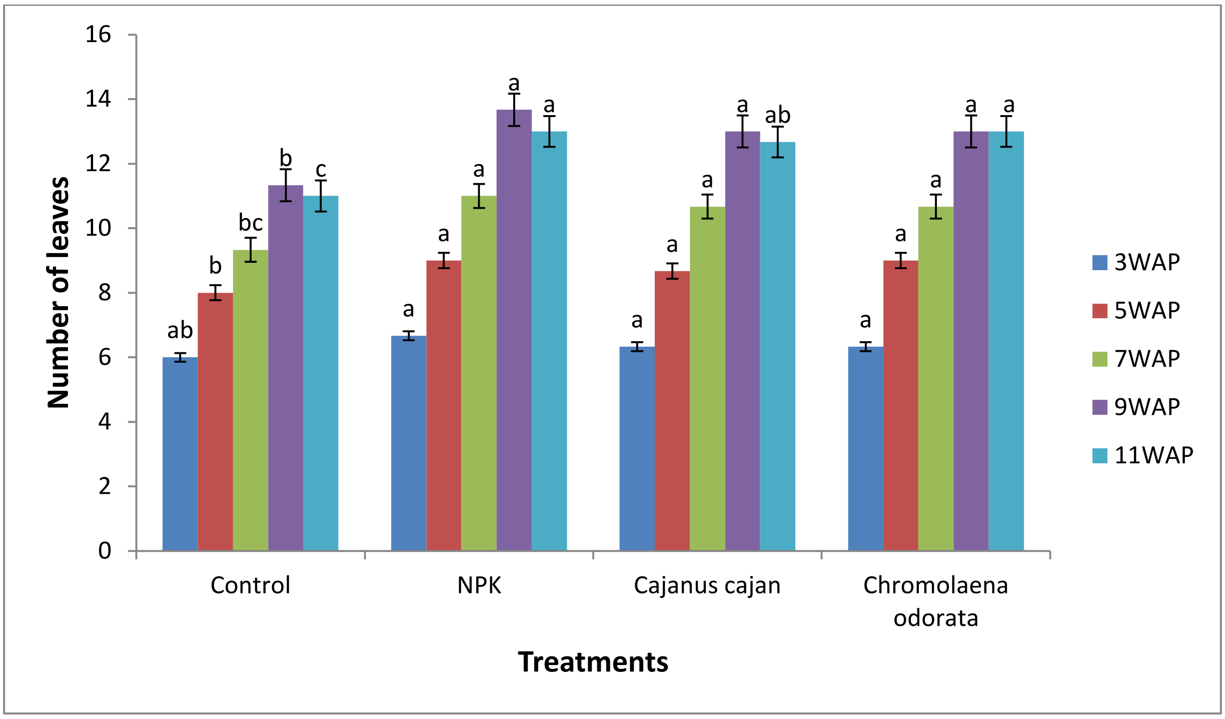

Figure 2: *The effects of mulches and NPK on the number of leaves at different stages of growth of maize in 2014*

Legend: WAP: Weeks after planting

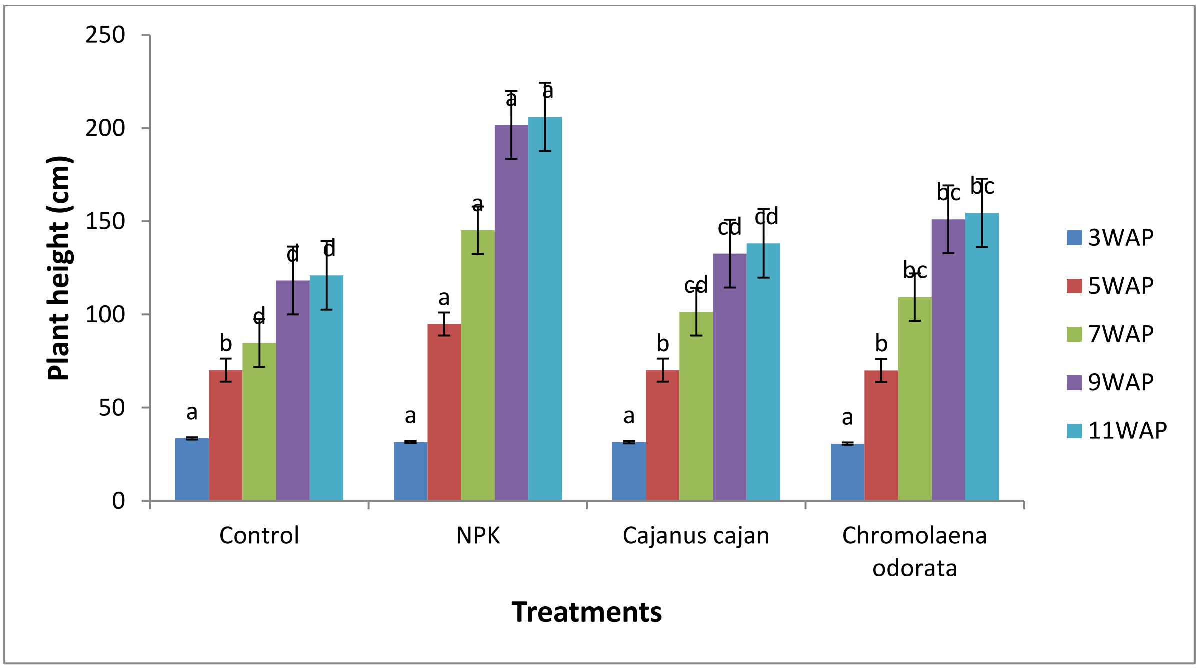

Figure 3: *The effects of mulches and NPK on plant height (cm) at different stages of growth of maize in 2013*

Legend: WAP: Weeks after planting

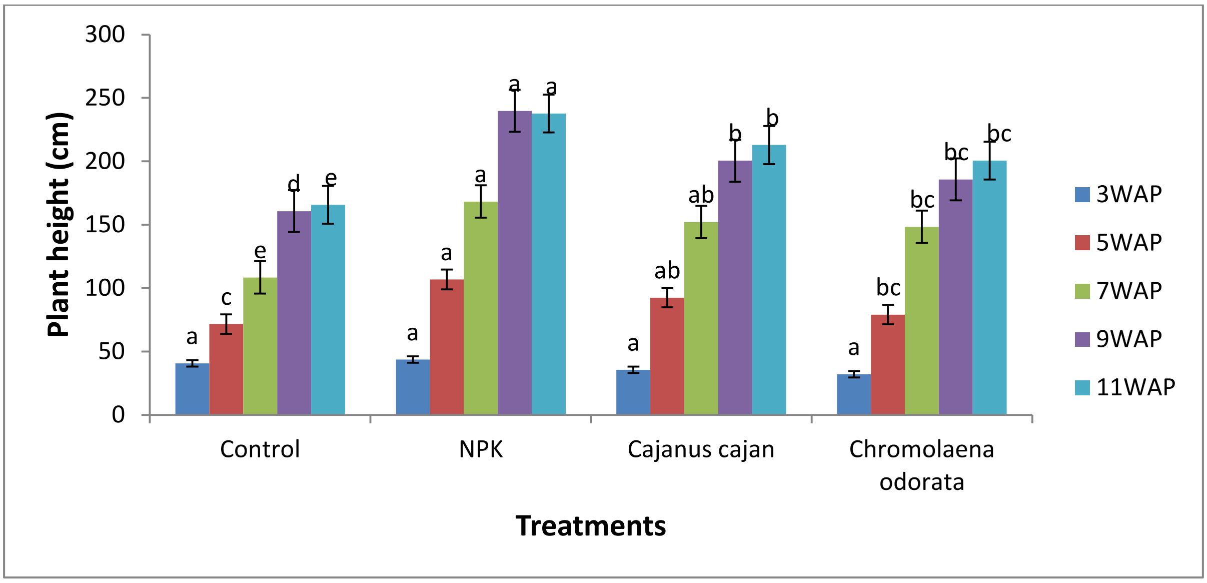

Figure 4: *The effects of mulches and NPK on plant height (cm) at different stages of growth of maize in 2014*

Legend: WAP: Weeks after planting

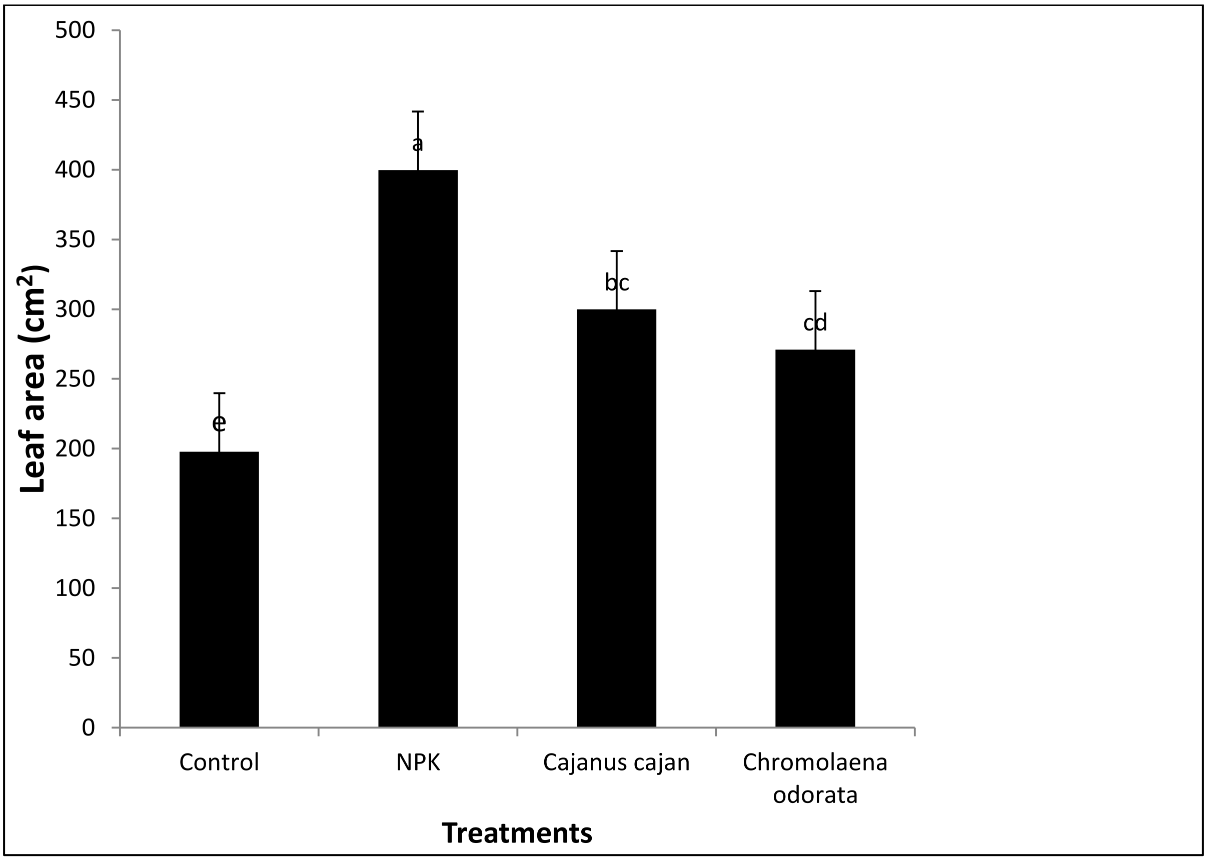

Figure 5: *The effects of mulches and NPK on leaf area (cm^2) at 8 WAP of maize in 2013*

Legend: WAP: Weeks after planting

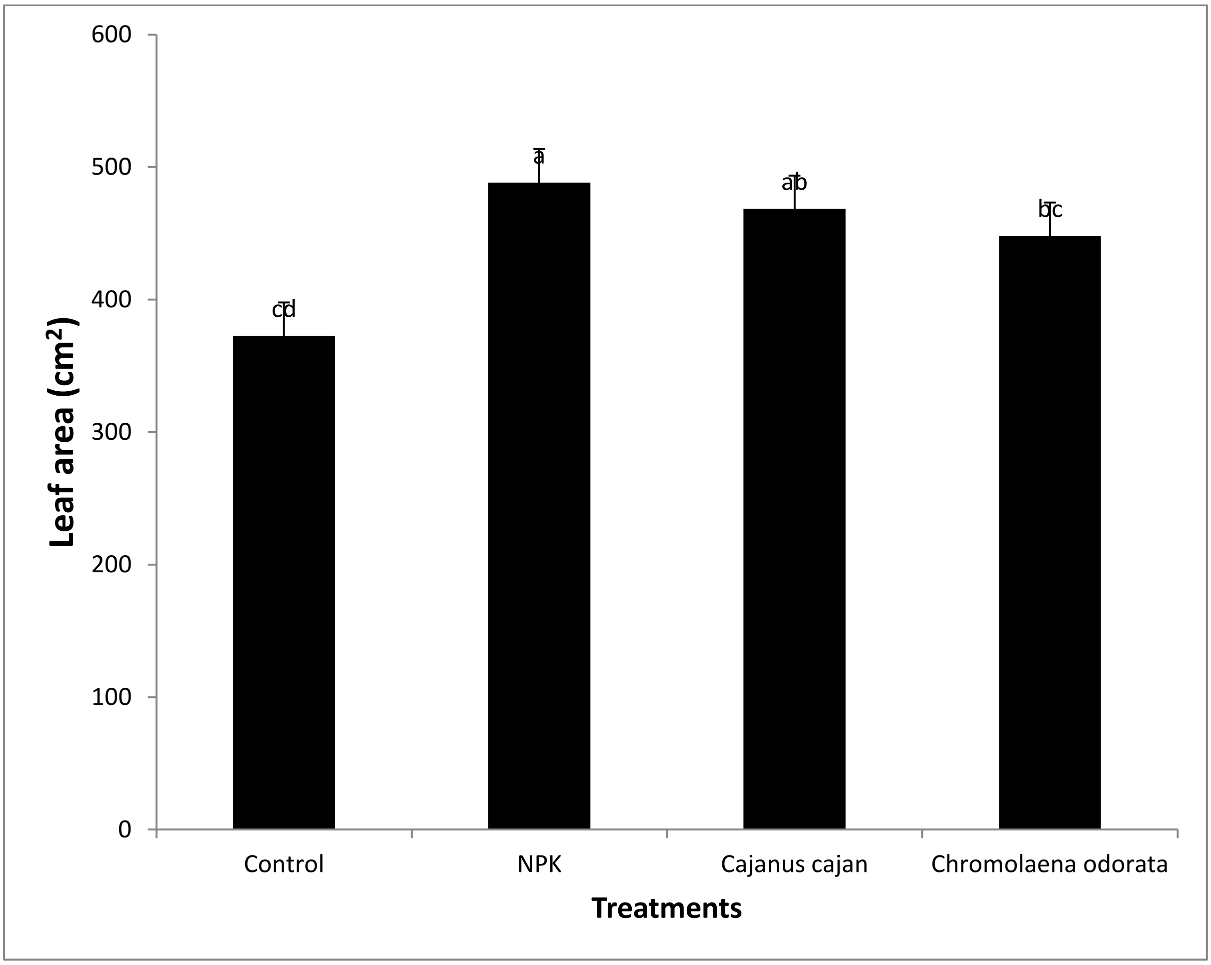

Figure 6: *The effects of mulches and NPK on leaf area (cm^2) at 8 WAP of maize in 2014*
Legend: WAP: Weeks after planting.

Table 4: Effects of mulches and NPK fertilizer on maize yield parameters at the end of 2013 cropping

Dry matter **Treatment**	**Grain yield ($t\ ha^{-1}$)**	**Biomass ($t\ ha^{-1}$)**	**Shelling Yield ($t\ ha^{-1}$)**	**Harvest percentage (%)**	**index (%)**
Control	0.98d	0.63d	3.05c	70.31ab	20.66bc
NPK (20:10:10)	2.32a	2.19a	7.55a	72.10ab	29.01ab
Cajanus cajan	1.65bc	0.93cd	4.84bc	68.59ab	19.21c
Chromolaena odorata	1.63bc	1.10cd	4.54bc	72.19ab	24.23bc

Means followed by the same letter within each column are not significantly different (P= 0.05) as indicated by Duncan's Multiple Range Test

Table 5: Effects of mulches and NPK fertilizer on maize yield parameters at the end of 2014 cropping

Dry *matter* Treatment	**Grain yield ($t\ ha^{-1}$)**	**Biomass ($t\ ha^{-1}$)**	**Shelling Yield ($t\ ha^{-1}$)**	**Harvest percentage (%)**	**index (%)**
Control	1.94d	1.23cd	4.98d	63.97c	24.65c
NPK (20:10:10)	3.18a	2.76a	9.12a	74.66a	30.26a
Cajanus cajan	2.94a	2.41a	7.58b	76.39a	31.79a
Chromolaena odorata	2.55bc	2.29ab	7.40bc	68.39bc	30.95a

Means followed by the same letter within each column are not significantly different (P=0.05) as indicated by Duncan's Multiple Range Test

Conclusion

This study has shown that the application of organic mulches such as *Cajanus cajan* and Chromolaena *odorata* has the potential of improving maize growth, biomass and yield which are comparable to inorganic fertilizers. It is pertinent to note that the organic mulches have the added advantage of improving soil quality and health which was observed in the increase in soil organic carbon and also its weed growth suppressing attribute which creates a conducive environment for maize production in the study area. It is recommended that small holder farmers should make use of *Cajanus cajan,* an easily available leguminous organic mulch applied at 5t/ha as an alternative to scarce and expensive recommended rates of NPK fertilizer or combined with reduced recommended rates of NPK fertilizer in the study area to boost maize production in their various holdings.

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Risk Assessment of Non-Uniformity in Irrigation and Fertilization for a Furrow Set Under Climate Uncertainties in the Sofia Field

Zornitsa Popova

N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection

1331 Sofia, 7 Shosse Bankya str.
Corresponding Author: Zornitsa Popova, e-mail: zornitsa_popova@abv.bg

Abstract

Water distribution could be quite non-uniform along the furrow length under surface irrigation. This "down field" disuniformity is usually combined with "inter-row" non-uniformity of irrigation water and nitrogen fertilizer distribution. Spatial variation of application depth and nitrogen (N) fertilization rate in the furrow plot produces yield, drainage and nitrogen losses. In addition to that, due to year-to-year variability of climate, regional irrigation depths range significantly (from 0 to 360 mm/season in the studied field). The objective of this paper is to study the impact of global nonuniformity of irrigation water and N fertilizer distribution within a furrow plot on yield, water and nitrogen losses when climate variability is taken into account. Six maize vegetation seasons with contrastive probability of exceedence of irrigation depth P_I are considered. Irrigation water is distributed according to six scenarios for "downfield" and "inter-row" non-uniformity by using the validated FURMOD model (Popova, 1990; 1992; Popova and Kuncheva, 1996). Nitrogen fertilization broadcast corresponds to two scenarios of lateral non-uniformity. The validated CERES-maize model (Jones and Kiniry, 1986;Gabrielle et al, 1995; Popova et al.1999; 2001-b; Popova and Kercheva, 2005) is applied with the different "climate-irrigation nonuniformity-fertilization nonuniformity" scenarios to simulate water&nitrogen cycle and crop growth on a daily basis in 30 representative points along "median", "high intake" and "low intake" furrows of the set. It is established that yield, water and nitrogen losses vary over uniformity scenarios and studied 30-year period. Combination of non-uniform irrigation/N-fertilization with the high irrigation demand seasons (having probability of exceedance P_I<11%) causes losses of yield by 2 to 14.5 % of potential maize productivity, irrigation water (up to 40-45% of applied depth) and nitrogen (up to 10-12% of N-rate). Model runs show that poor distribution uniformity of irrigation water and N fertilizer should be maintained especially in the case of high irrigation requirements. Different strategies aiming at reduction of heterogeneity sources of "inter-row" and "down-field" uniformity of water distribution and fertilizer broadcast are recommended.

Key words: Climate variability, Furrow irrigation model, Nonuniformity of Water, Nonuniformity of Nitrogen, CERES-maize model, Environmentally oriented strategies, Scenario analyses, N-leach, Crop production.

Introduction

Furrow irrigation has been a most wide–spread irrigation method in Bulgaria. It used to be applied over 70% of the irrigated area in this country, i.e. on 0.56 mil. ha in the 80-ies. Nowadays, due to low cost and energy requirements, it is becoming again an economic feasible perspective for irrigation under the conditions of market economy. Non-uniformity of water distribution is one of the basic features for evaluation and improvement of furrow (Varlev, I., 1976; Popova et al., 1998) and sprinkler (Paz et al. 1998) irrigation systems. Well-known fact is that water distribution is quite non-uniform along the furrow length under surface irrigation. This “down field” disuniformity is usually combined with “inter-row” non-uniformity in irrigation water and nitrogen fertilizer distribution (Davidov 1981; Marinov et al.,1985; Popova, 1990; 1991; 1992; Mailhol and Gonzales, 1993; Popova and Kuncheva,1996; Burt et al., 1997; Clemmence et al., 1997; Shahidian et al.,1998; Popova et al.,2005; Crevoisier et al., 2008). References prove that failure to take into account non-uniformity of water&fertiliser distribution should have been related to considerable errors when studding water and nitrogen cycle under furrow irrigation on a cracking soil. Spatial variation of application depth and fertilisation rate in the plot provokes on the other hand non-uniform yield production. There are a number of coefficients that characterise the uniformity of water distribution but not the variability of the resulting yield (Christiansen, 1941). Other numeric characteristics evaluate the impact of irrigation&fertilisation non-uniformity on yield loss by using second-degree polynomial “water/nitrogen-yield” relationships (Howell, 1964; Varlev, 1976; Varlev, 1988; Popova, 2008). Yield losses due to non-uniform irrigation depend also on the wetness of vegetation season and required irrigation depths (Varlev and Popova, 1999; Popova, 2006). Risk of yield losses and environmental pollution associated with climate variability and management practice is analysed by model simulation during the recent decades (Algozin et al., 1988; Popova et al. 1995; Gabrielle et al., 1995; Popova et al., 2001-a; Popova and Kercheva, 2004; 2005; Popova, 2008). Powerful agronomic tools, as CERES (Jones and Kiniry. 1986), WAVE (Vancloster, 1994) and other dynamic models deal in a point scale with the interactions between cropping methods, fertilisers and irrigation in the “ground water-soil-crop-atmosphere” system. One-dimensional models do not take into account though phenomena that are inherent to the plot, as the non-uniformity in applying irrigation water and fertilisers. This paper deals with longitudinal and lateral non-uniformity of irrigation water&nitrogen fertiliser distribution in a furrow set under maize grown on a Chromic Luvisol soil, Chelopechene field, Sofia region. Unlike studies on yield losses due to non-uniform irrigation and fertilisation, which have mostly economical dimensions, this analysis in addition evaluates quantitatively the negative impact of Global non-uniformity on environment and crop productivity in the presence of year-to-year variability&change of climate and maize irrigation requirements. The FURMOD (Popova, 1990; 1991; 1992; Popova and Kuncheva, 1996) and modified CERES-maize (Gabrielle et al., 1995; Popova et al., 1999; 2001-b; Popova and Kercheva, 2005) models, being previously calibrated and validated with data from field observations at plot, parcel and lysimeter scale, are presently used to estimate deep percolation, runoff and yield losses for a set of simultaneously irrigated furrows. The paper compares the consequences of non-uniform distribution of irrigation water and nitrogen fertiliser in a plot scale with the performances of improved surface irrigation technologies with uniform inter-row stream advance and fertiliser broadcast.

Material and Methods

Precise irrigation scheduling of maize grown on a Chromic Luvisol soil in Chelopechene Experimental Field, Sofia region for a long-term 1960-1990 period, as determined by Popova and Kercheva (1999, 2001-a, 2002, 2004, 2010), is used to obtain probability curve of occurrence of an irrigation depth. Data about climate (potential evapotranspiration of grass reference surface and precipitation on a daily basis), crop (duration of growth stages, K_c factors) and soil (total available soil water-$\boldsymbol{TAW}$, that is 140 mm/m, and maximum rain infiltration rate of 150 mm/day) are input for CROPWAT programme (Smith, M. et al 1992). Optimised K_c values under Bulgarian conditions (Popova and Feyen, 1996), respectively 0.3 for initial, 1.1 for mid season and 0.6 for late season growth stages, are constant input for the runs of the program. The irrigation is scheduled whenever the critical soil moisture level, that is $0.4\boldsymbol{TAW}$ for development and mid season stage and 0.8***TAW*** for late season, is reached. Application depth is set equal to the depleted soil water in the root zone. Seasonal irrigation depths vary from 0 to 359 mm over the studied period. The number of water application is 0-2 in wet irrigation seasons, 3-4 during medium ones and 4-7 in dry ones. Obtained probability curve is validated by comparing it to independent experimentally based estimates of 180, 240 and 300 mm/season for probability of exceedance of the irrigation depth (P_I, %) respectively 50%, 25% and 10% (Zahariev et al, 1986). Six representative maize vegetation seasons with contrastive irrigation requirements (3 %< $\boldsymbol{P_I}$ <97 %) are chosen for the further analyses.

Application depths are distributed over a furrow plot according to six scenarios of irrigation uniformity corresponding to Christiansen coefficient (C_u, %) within the range $53<C_u<90\%$. Spatial mathematical description of intake depth along the non-homogeneous furrows is made by FURMOD model (Popova, 1990; 1991; Popova and Kuncheva, 1996). The model calculates in relative terms water distribution&losses for a wide range of conditions in irrigation practice, as application time and depth, soil infiltration parameters, water deficit in the root zone, “downfield” and “inter-row” non-uniformity of water distribution. It is assumed that equal irrigation streams are simultaneously delivered / stopped at the heads of the furrows. Stream advance L, when arranged in descending order, is approximated by a straight line (Figure 1) with a coefficient K_{nun} (Varlev, 1988), defined as:

$$K_{nun} = (L_{max}-L_{min})/L_{med} \qquad (1)$$

, where L_{max}, L_{min} и L_{med} are, respectively, the wetted lengths of the least (No5), most (No1) and median (No3) permeable furrow read from the approximated line of stream advance (Figure 1) and K_{nun} is the coefficient of non-uniformity of stream advance.

The duration of irrigation event is defined as the relative extension of application time I, which represents the additional irrigation time t_{ad} after the irrigation stream has reached the furrow tail in the “median” furrow t_l:

$$I = t_{ad} / t_l \qquad (2)$$

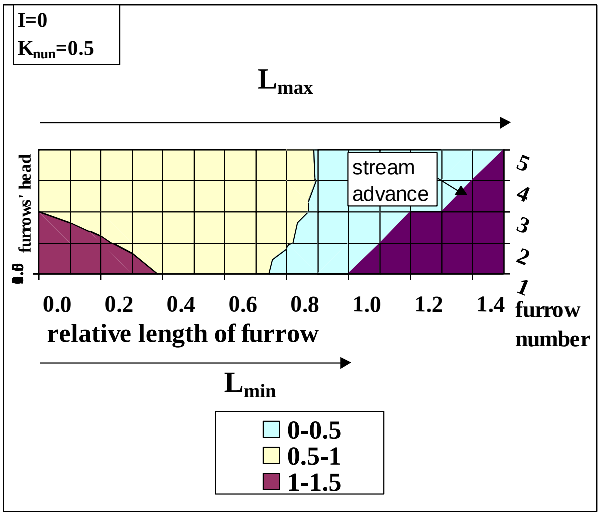


Figure 1. *Distance of advance in high intake (No1), median (No3) and low intake (No5) furrow, arranged in a descending order and lines of equal infiltrated depth for elapsed time t_l (I = 0) and K_{nun} = 0.5 in relative terms.*

The equal volumes of water, delivered at the heads of the furrows, are distributed along the furrow length L as described by the following equation:

$$m_x = 1.5m_{av}\,(1-0.86x/L)^{0.5} \qquad (3)$$

,where m_{av} is the average depth of water taken by the soil over the distance of stream advance L.

The furrow length L is the accepted unit of length. The required depth of water for filling up of the root zone to FC - m_{req}, which is retained at the head of the median furrow (No3) for time t_l, is the accepted unit of depth.

Intake depth is calculated using the time based functions of infiltration rate K_t (Kostiakov, 1932):

$$K_t = K_1 / t^{\alpha} \tag{4}$$

and stream advance X in the furrow by Equation (5):

$$X = L_1 \; t_X{}^{n} \tag{5}$$

where K_t is the intake depth after elapsed time t (m/s); K_1 the coefficient (m/s$^{1-\alpha}$); X the advance distance (m); L_1 the distance of stream advance for the first elapsed unit of time (m); t_X the advance time to position X (s); α and n are the empirical exponents.

Despite the fact that exponents α and n (Equations 4 and 5) do not remain the same throughout the irrigation season, in this study it is assumed that they are constant ($\alpha = 0.7$ and $n = 0.8$) in the median furrow. Assumed values are within the range of those frequently observed in the field (Popova, 1990; 1992).

The intake depth is calculated along the simultaneously irrigated furrows according to six non-uniformity scenarios. Water distribution is estimated for two values of irrigation duration: one I = 0.8 (Equation 2), when the average intake depth is equal to the required depth m_{req} and another one I = 0, when 70% of required irrigation depth is distributed. Three cases of lateral non-uniformity: $K_{nun} = 0$; $K_{nun} = 0.5$ и $K_{nun} = 1$, provoked by the differences of stream advance, are combined with each irrigation duration.

The treatments of irrigation nonuniformity are studied under different fertilisation application. Nitrogen fertilisation rate (200 kg N/ha) is applied over the furrow plot according to two scenarios: one of ideal N-split and distribution uniformity (coefficient of N variation $C_v = 0$ %) and another practically oriented one ($C_v = 30$ %). Total N-dose is split to 1/3 in spring and 2/3 just before the most intensive phases of crop development with the first fertilisation treatment. The second one consists of single N-application in spring with certain inter-row nonuniformity of distribution, as illustrated in Figure 2. The curvilinear diagram in the figure and the range of coefficient of variation of surface N-distribution in practice ($C_v = 25$-30 %) are established by researchers in the Institute of mechanisation of agriculture (Marinov et al., 1985). The second degree polynomial distribution line is approximated by a step line of three N-rates. The risk assessment analyses are carried out when the representation of each rate over the area of simultaneously irrigated furrows is taken into account.

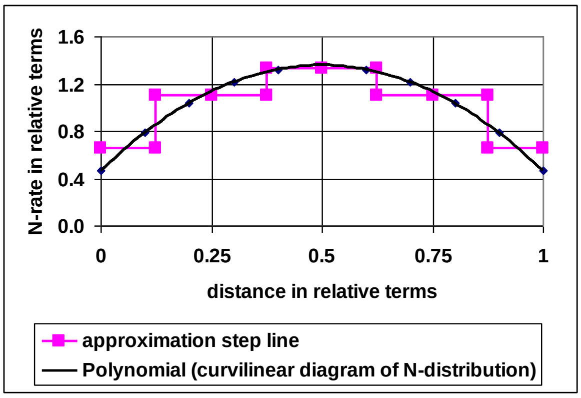
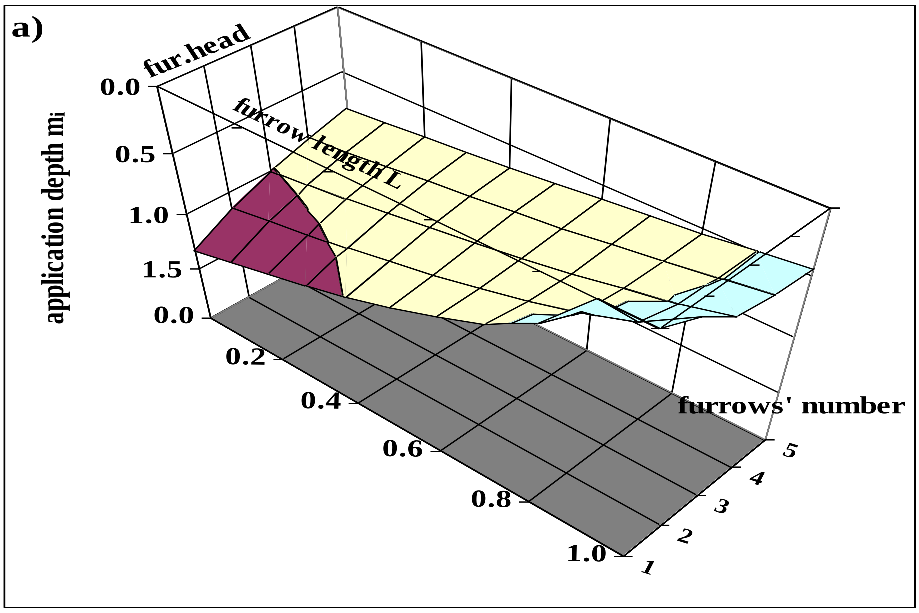


Figure 2. *Inter-row distribution of N-rate over the distance covered by a run of the broadcasting implement in use in Bulgaria.*

Validated CERES-maize model (Jones C.A., J.R. Kiniry. 1986; Gabrielle et al, 1995, Popova et al.1999; Interim and final reports of INCO-COPERNICUS Project 1997-1999; Popova et al. 2001-b; Popova and Kercheva, 2002; 2005) is applied for 30 representative points in the irrigation plot (by 6 along the length L in 5 furrows). Crop growth and fate of water and nitrogen in the non-homogeneous system are simulated for different “climate-irrigation nonuniformity-fertilisation nonuniformity” combinations. The model used to be extensively calibrated and validated previously against three-year data observed in irrigated and rainfed plots and lysimeters in Chelopechene field (Sofia region, Bulgaria). Calibration is carried out for a wide range of water stress and N-split condition at non-limited fertilisation level (200 kg N/ha) and then validated with independently obtained data. As a result the model estimates reliably crop yield (in dry weight of ears), water and nitrogen contents in the soil and crop uptake, water drainage and nitrogen leaching linked to different irrigation and fertilisation treatments and climate. In these analyses it is assumed that crop parameters are constant within the frames of the considered plot, over the years and uniformity scenarios. Yield losses and deviation of drainage and nitrogen leaching within the furrow plot due to nonuniformity of irrigation water&fertiliser distribution is related to probability of exceedance of irrigation depth P_I. The latter characterises the wetness of the irrigation season over a 30-year period (1960-1990).

Results and Discussion

According to the assumptions referred above, distribution of relative intake depth $\mathbf{m_i}$ over the area of furrows’ set depends only upon the combination of the parameters of longitudinal (I, Equation 2) and lateral (K_{nun}, Equation 1) nonuniformity. A spatial 3D representation of $\mathbf{m_i}$ distribution for four of the studied nonuniformity scenarios is given in Figure 3. Figure 3-a illustrates the situation from Figure 1 when relative extension of application time I is 0 and coefficient of nonunifomity of stream advance K_{nun} is 0.5. Coefficient of nonuniformity C_u (Christiansen, 1941) is 69%. Figure 3-b presents the distribution of the same quantity of irrigation water (I = 0) but with maximum inter-row disuniformity ($K_{nun} = 1$) corresponding to $C_u = 53$ %. High intake furrow with the shortest stream advance is No1, low intake one with the longest stream advance is No5 and median furrow is No3. Figs.3-c and 3-d illustrate the situations of the same lateral nonuniformity when 50 % more water is applied by extension of application time to I = 0.8 and thus improving the uniformity coefficient to C_u =83 % and C_u =67 %. The area of insufficient water supply ($m_i < m_{req}$) is presented in light yellow and blue colours while the remaining part of the plot, coloured in darker brown and purple, signifies deep percolation losses.



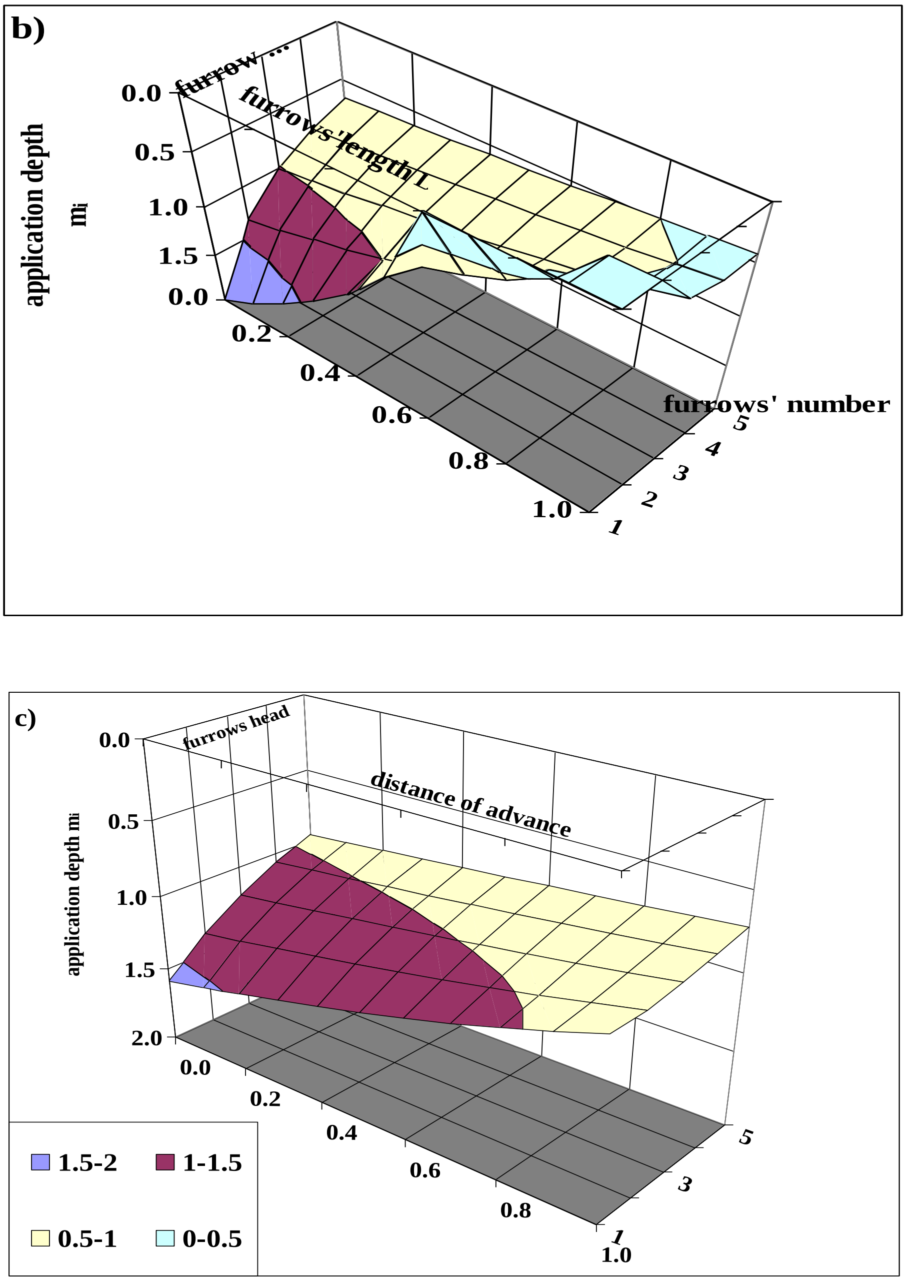


Figure 3. *Intake depth in relative terms* m_i *along median (No3), high intake (No1), low intake (No5) furrow for different scenarios of nonuniformity of irrigation water distribution: a)* $I = 0$ *(Eq.2),* $K_{nun} = 0,5$ *(Eq.1),* $C_u = 69\%$; *b)* $I = 0$, $K_{nun} = 1$, $C_u=53\%$; *c)* $I=0.8$, $K_{nun}= 0,5$, $C_u = 83\%$; *d)* $I = 0.8$, $K_{nun} = 1$, $C_u = 67\%$.

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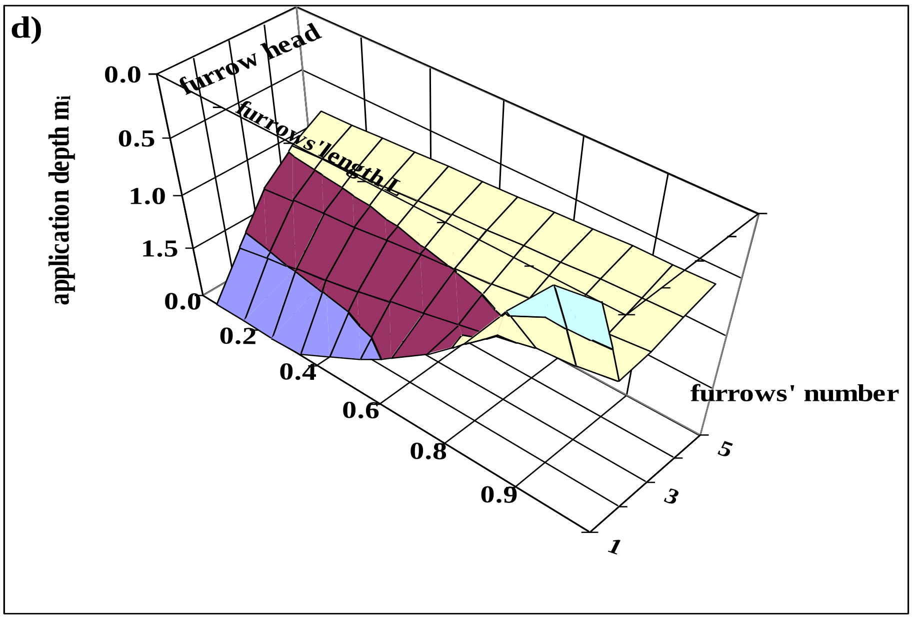

Figure 3. (Continued)

Scenarios of nonuniformity in irrigation water distribution (Figure 3) are combined with the different climate and N fertilisation uniformity treatments (Figure 2). Impact of “low uniformity” irrigation ($I = 0$, $K_{nun} = 1$, $C_u = 53$ % in Figure 3-b) under split uniform fertilisation ($C_v = 0$) on yield, water and nitrogen losses is different over the years. This scenario presupposes that irrigation streams do not reach the tail of “high intake” furrows No1 and No2 and some part of the plot remains rainfed. It means that nitrogen use efficiency is low there in dry irrigation season ($P_I = 3$-11%). As a result the yield is uniform within the area of the plot only after wet irrigation period ($P_I = 77$ %), it varies moderately ($C_v = 4$-8 %) when $P_I = 48$-60% (Figure 4-a) and essentially ($C_v = 19$-26%) after dry seasons with $P_I = 3$-11 % (Figure 4-b).

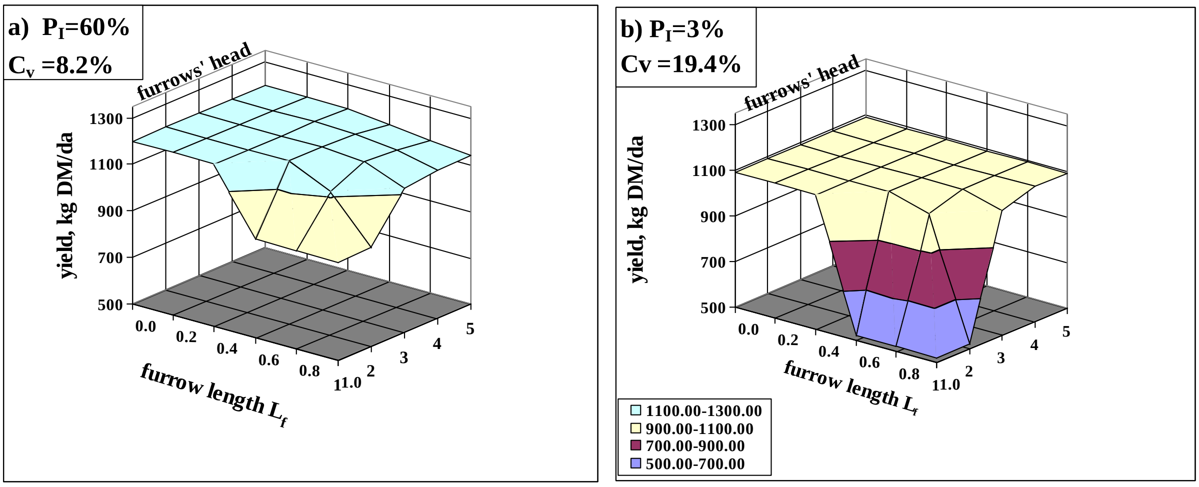

Figure 4. *Yield distribution along median (No3), high intake (No1), low intake (No5) furrow under “low uniformity” furrow irrigation scenario ($I=0$, $K_{nun}=1$, $Cu=53\%$) and split uniform fertilisation ($C_v=0$) in case of: a) average irrigation season ($P_I=60\%$) and b) dry irrigation season ($P_I=3\%$) .*

Figure 5 represents production losses due to nonuniformity of irrigation water distribution dependent upon required irrigation depth and its probability of exceedance P_I.

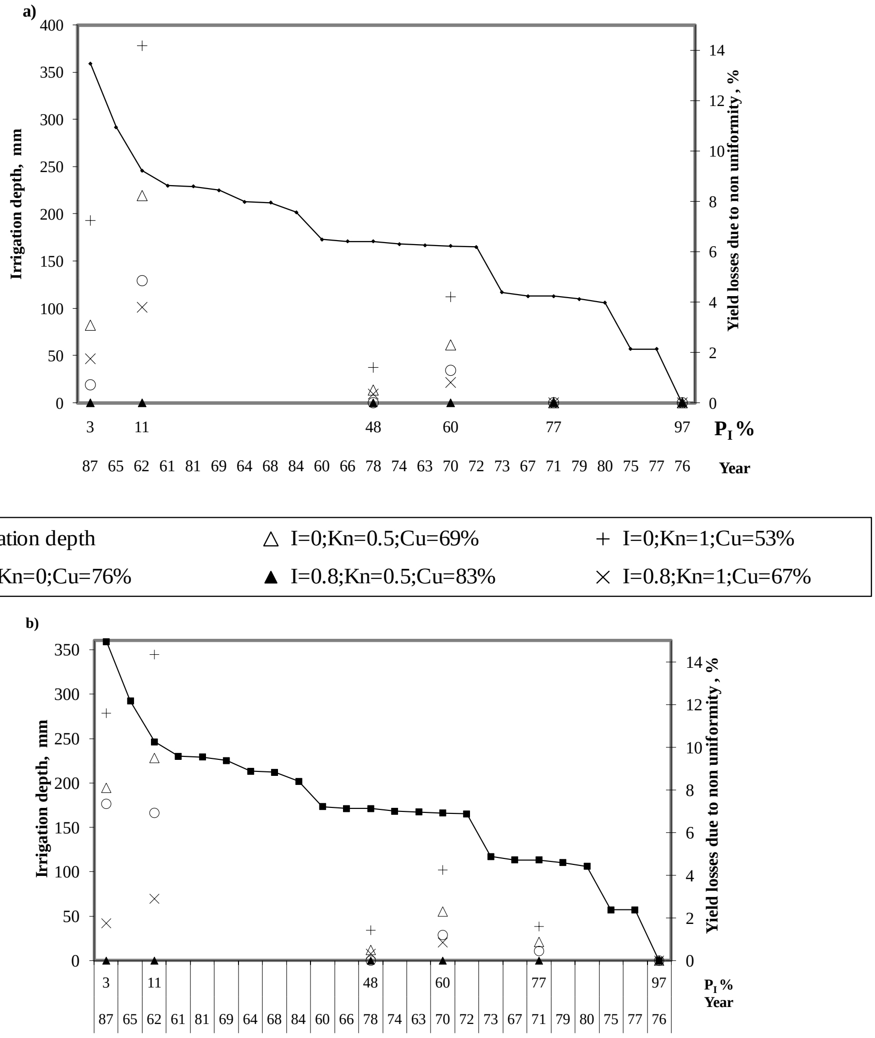

Figure 5. *Yield losses due to irrigation water nonuniformity dependent on probability of occurrence of an irrigation depth P_I, Chromic Luvisol soil, Sofia region under: a) split uniform (C_v=0 %) fertiliser application and b) single nonuniform (C_v=30 %) fertiliser spring broadcasting, 1960-1990.*

Figure 5-a illustrates the results obtained under split uniform ($C_v = 0\%$) N-application and Figure 5-b those valid for single nonuniform ($C_v = 30\%$) fertilisation broadcast according to the diagram in Figure 2. As a consequence of irrigation “low uniformity” treatment of I = 0; $K_{nun} = 1$ and $C_u = 53\%$ (the water distribution situation in Figure 3-b), yield losses in % of the yield, which should have been harvested with uniform irrigation/fertilisation, are practically 0-2 % after wet vegetation periods ($P_I = 77$ %), they reach 1.8-4.2 % over average ($P_I = 48$-60%) and augment up to 7.3-14.6 % in the very high and high irrigation demand years of $P_I = 3$-11 % (“+”-symbols plotted in the secondary Y-axis in Figure 5). The concrete years involved in these analyses are superposed to the probability P_I of irrigation depth plotted in the X-axis. Yield losses could be reduced up to two folds (open “Δ” symbols in Figure 5-a) at the same level of areal average water (I = 0) and nitrogen (200 kg N/ha) supply by improving the “inter-row” uniformity of stream advance to $K_{nun} = 0.5$ (the situation in Figure 3-a) and fertiliser broadcast to $C_v = 0$ %. When distances of stream advance along the simultaneously irrigated furrows are completely equal ($K_{nun} = 0$), as well as the fertilisation rates distributed across the plot, maximum yield is produced with minimum irrigation water supply (open “o”-symbols, Figure 5-a).

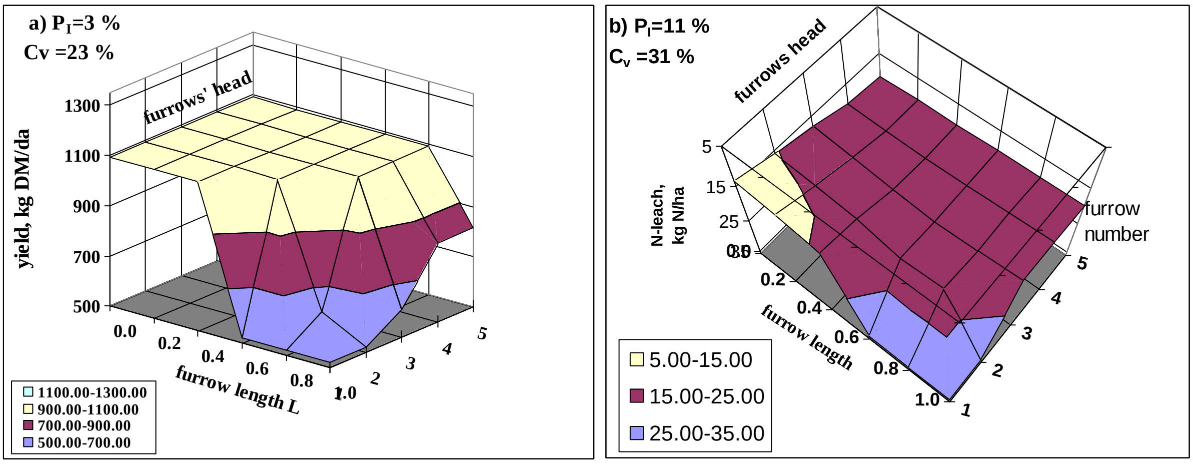

Figure.6. *Consequences of combined “low uniform” furrow irrigation (I=0, Кнер=1,Cu=53%) and fertilisation (Cv=30%) scenarios for maize plot with a dry irrigation season (P_I=3-11%) for : a) Yield distribution b) Variation of N-leach totals for “Oct-Apr” fallow state period.*

Combination of nonuniform fertilisation (C_v = 30%) and irrigation (C_u = 53 %) with the very dry irrigation season of 1987 (P_I = 3 %) leads to additional yield losses (Figure 5-b) due to the reduction of crop productivity along the tail of all furrows (Figure 6-a).

The drier is the irrigation season the higher is also the potential environmental risk due to irrigation&fertilisation nonuniformity. As a result of high residual soil N-NO_3 after a dry season (1962, P_I = 11 %), hazardous N-leaching may arise in case of precipitation extremes in fallow state especially over the rainfed part of the “high intake” furrows No1 and No2 (Figure 6-b).

Figure 7 illustrates the overall environmental impacts of the “low uniformity” irrigation treatment (I = 0; K_{nun} = 1; C_u = 53%) under uniform (“o”-symbols) and nonuniform (“x”-symbols) fertilisation scenarios related to the probability of occurrence of an irrigation depth P_I. Mean and standard deviation (STDEV) bars of drainage and N-leaching totals for May-September period (Figure 7-a) coincide for both fertilisation scenarios except for the N-leach in the extremely wet rainfed vegetation period for 1976 (P_I = 97%). It is obvious that STDEVs in Figure 7-a depend upon the wetness of the irrigation season. In moderately wet 1971 (P_I = 77%) drainage and N-leaching are uniform across the plot. STDEV bars augment when the season in getting drier and reach 98 mm for the drainage and 4 kg N/ha for the leaching in 1987 when P_I = 3%. The same tendencies hold true for the deviation of residual N-NO_3 in the soil, which ranges from 10 kg N-NO_3/ha (1971, P_I = 77%) up to 50-60 kg N-NO_3/ha in the dry irrigation seasons of 1987 and 1962 (P_I = 3-11%) (Figure 7-b). The drier is the irrigation season the higher is the mean residual soil N-NO_3. Nonuniformity in fertilisation produces additional threat to environment since values of mean residual soil nitrate in the furrow set are 10-15 kg N-NO3/ha higher than those associated with uniform fertilisation scenario.

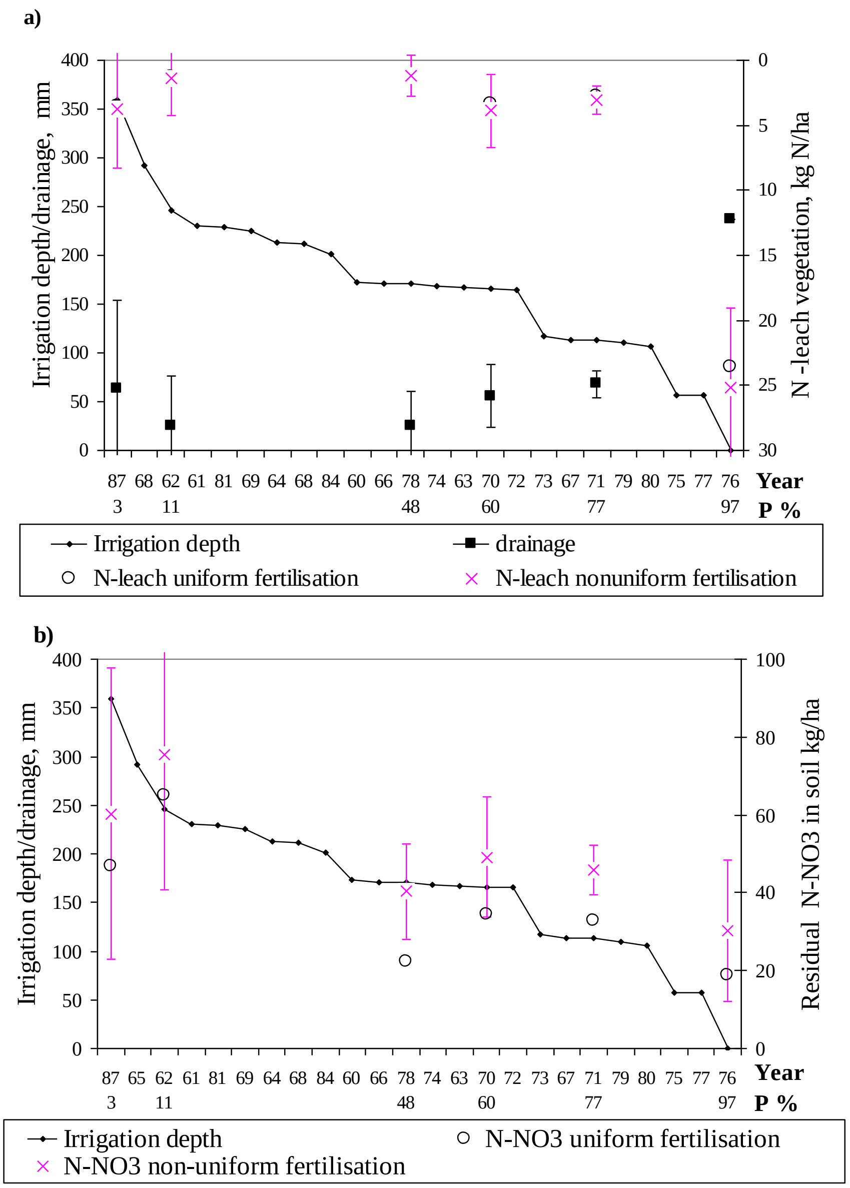

Figure 7. *Impact of irrigation "low uniformity" treatment (I=0 K_{nun}=1 C_u=53%), nonuniformity in fertilisation and probability of occurrence of an irrigation depth (P_I) upon mean and STDEV relative to: (a) drainage and N-leaching totals for May-September period; (b) residual N-NO_3 in the soil, 1960-1990.*

Adverse impact of furrow irrigation on ecology is mitigated at the same level of irrigation water supply (I = 0) in the case of ideal lateral uniformity in irrigation (K_{nun} = 0) and fertilisation (C_v = 0) according to the results plotted in Figure 8. STDEVs of drainage&N-leaching (Figure 8-a) and residual soil N-NO_3 (Figure 8-b) are substantially reduced (2-3 folds) if compared with the respective graphs in Figure 7. The consequences of nonuniformity (C_v = 30%) in N-broadcasting on mean residual N-NO_3 in the soil under improved irrigation uniformity (C_u = 76 %) (Figure 8-b) is similar to those in Figure 7.

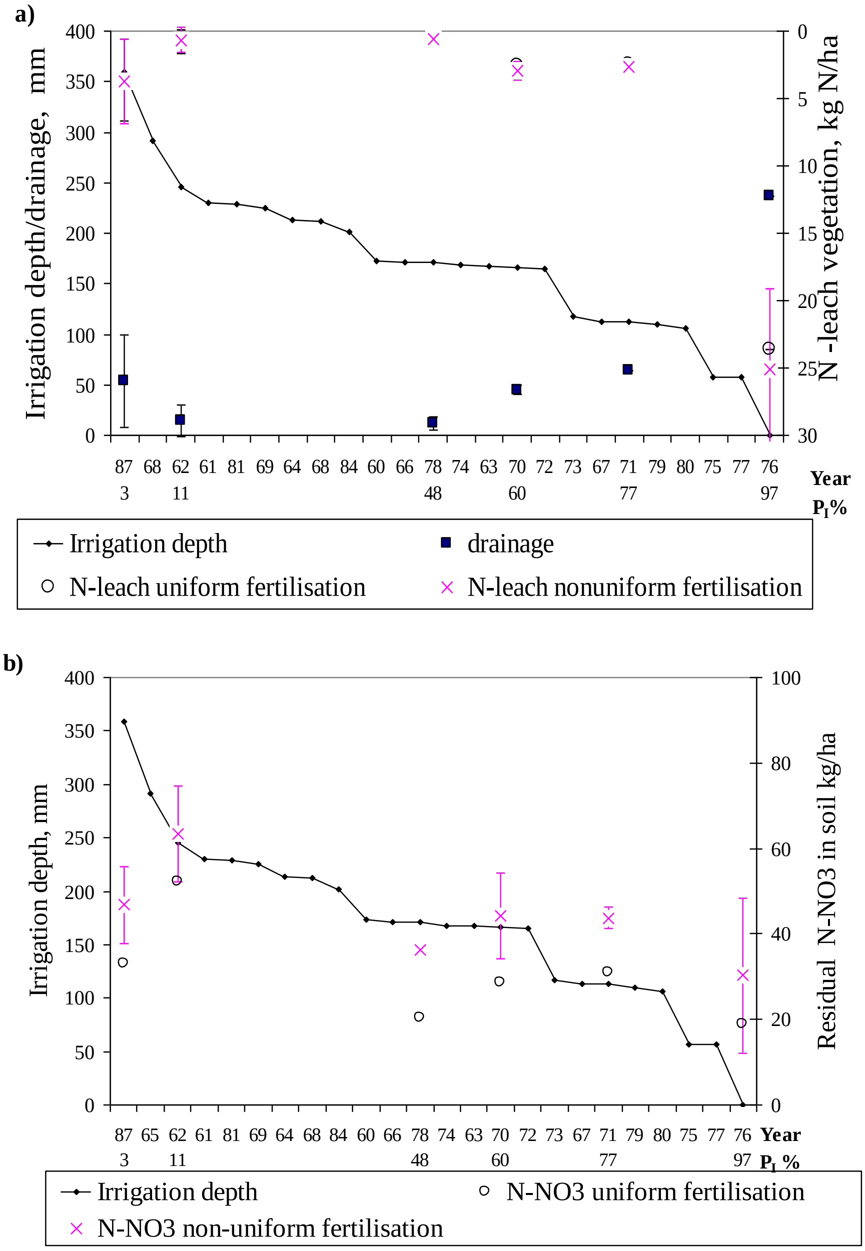

Figure 8. *Impact of irrigation "high- uniformity" treatment (I=0 Knun=0 Cu=76 %), nonuniformity in fertilisation and probability of occurrence of an irrigation depth (P_I) upon mean and STDEV relative to: (a) drainage and N-leaching totals for May-September period and (b) residual N-NO3 in the soil, 1960-1990.*

Regarding surface irrigation practice, the coefficient for non-uniformity of stream advance K_{nun} (Eq.1) ranges within the limits 0.4 - 1.0 (Popova, 1991; 1992; Popova and Kuncheva, 1996; Varlev et al., 1998). The situations of ideal lateral uniformity of stream advance ($K_{nun} = 0$) and N broadcasting ($C_v = 0$) are exceptional. These scenarios are only used as a basis of comparison in the study.

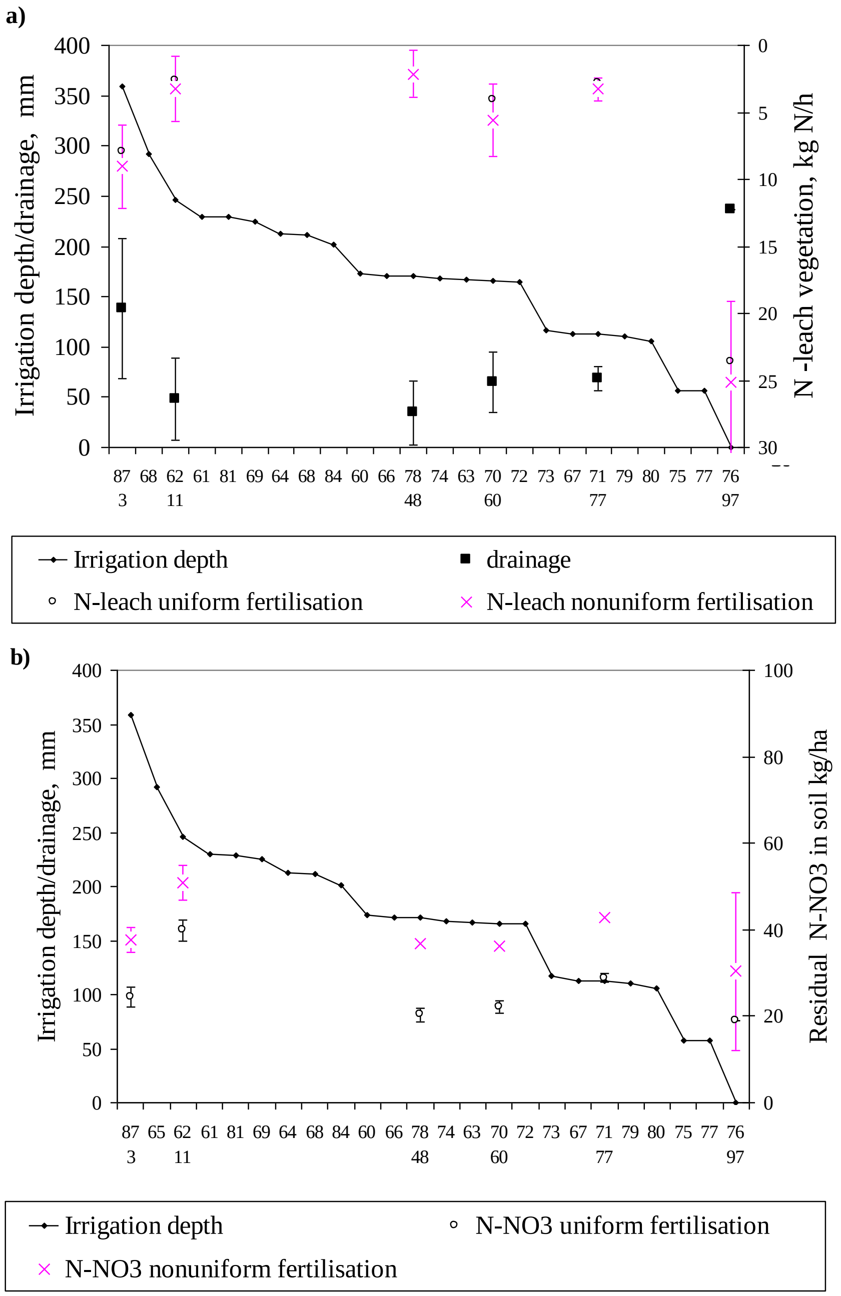

Figure 9. *Impact of irrigation "high-uniformity" treatment ($I=0.8$ $K_{nun}=0.5$ $C_u=83$ %) , nonuniformity in fertilisation and probability of occurrence of an irrigation depth (P_I) upon mean and STDEV relative to: (a) drainage and N-leaching totals for May-September and (b) consequent residual N-NO_3 in the soil, 1960-1990 .*

Yield loss due to non-uniformity of irrigation water distribution drops from 14.2% to 0 % by extending the application time to I = 0.8, i.e. by applying 50 % more irrigation water, and combining it with a real world 'inter-row" nonuniformity of $K_{nun} = 0.5$ (▲- symbols in Figure 5). Such choice however is possible if the price of water is relatively low and/or if runoff is reused. Figure 9 shows however that this practically oriented irrigation scenario is associated with environmental hazards due to double deep percolation (37-45% of the applied irrigation water) and N-leach (up to 10-12% of the applied N) in dry and average irrigation seasons of $P_I < 77$ % when compared to the results in Figure 8-a.

Total drainage over "May-September" is 70 mm on the average in 1970 ($P_I = 60\%$) and reaches 130 mm in the driest irrigation season of 1987 having $P_I = 3$ % (Figure 9-a). When I = 0.8 (Eq. 2), residual soil N-NO_3 is the least and practically constant over the plot and analyzed years: 20-35 kg N-NO_3/ha for split uniform fertilization scenario and between 35-45 kg N/ha for single nonuniform broadcast of the N-rate (Figure 9-b).

In the case of extreme seasonal precipitation events (1976, P_I = 97%), 23 and 25 kg N/ha are leached respectively under uniform and nonuniform fertilization scenarios. N-leach does not vary under uniform fertilisation and it deviates by 6 kg N/ha due to nonuniform fertilisation treatment nevertheless that the drainage is completely uniform across the plot in this season (Figures 7a, 8a and 9a).

Surface irrigation performances are improved in Bulgaria during the last decades. Modernised equipment for uniform stream delivery at the furrows' head, as flexible gated pipelines, has been disseminated. The new method of surge irrigation has been studied and practised in this country for 45 years (Varlev, 1971, Popova et al., 1994, Varlev et al., 1998 and 2011). In addition to water saving effect, it mitigates the variability of infiltration characteristics across the field and reduces substantially lateral non-uniformity of stream advance. Another surface irrigation practice is the cutback of streams delivered in the "low intake" furrows (No4 and No5 in Figures 1 and 3) or compaction of the "high intake" furrows (No1 and No2). Better distribution of nitrogen fertiliser is achieved by optimising the distance between two adjacent runs of the broadcasting implement used that could range between 6 and 30 m depending on the grown crop in Bulgaria (Marinov et al.1985).

Conclusions

The impact of nonuniformity in irrigation and fertilisation on yield, water and nitrogen losses is studied for maize grown on a Chromic Luvisol soil in six vegetation seasons of contrastive irrigation requirements, which are representative over a thirty-year period in Sofia field. Application depths are distributed over a furrow plot according to six scenarios of irrigation uniformity corresponding to Christiansen coefficient (C_u, %) within the range 53 % <C_u< 90 %, three of which are discussed in details. Description of intake depth along the non-homogeneous furrows is made by FURMOD model (Popova, 1990; 1991; Popova and Kuncheva, 1996), which calculates in relative terms water distribution for a wide range of conditions in irrigation practice, as application time and depth, soil infiltration parameters, water deficit in the root zone, "downfield" and "inter-row" non-uniformity of water distribution. Each treatment of irrigation nonuniformity is combined with two scenarios of nitrogen fertilisation: one of ideal N-split and uniformity of distribution (C_v=0) and another one reflecting the real world nonuniformity of N-broadcast (C_v=30%). Crop growth and fate of water and nitrogen over the furrow set are simulated in 30 representative points by the validated CERES-maize model. Analyses of the risk due to non-uniform irrigation and fertilization in the context of climate uncertainties are organized in three aspects:

1. **Yield losses:**

Yield losses in % of the yield, which should have been harvested under uniform irrigation, depend significantly on water distribution nonuniformity and wetness of the irrigation season. In case of "low uniform" irrigation (I=0; K_{nun}=1; C_u=53 %) and split uniform N fertilisation (C_v=0), they are practically 0 % after moderately wet irrigation periods (P_I=77 %) and augment up to 7.3-14.2 % after dry seasons (P_I=3%-11 %) (Figure 5-a). Yield losses could be reduced up to two folds at the same level of mean water and nitrogen supply by improving the lateral nonuniformity of stream advance from K_{nun}=1 to K_{nun}=0.5. When applying 50% more irrigation water (I=0.8) with a sufficient stream advance uniformity (K_{nun}<0.5) yield losses do not depend upon climate variability. Such irrigation practice however is economically feasible only if the price of the water is relatively low and/or if the runoff is reused.

Combining nonuniform fertilisation (C_v=30%) and irrigation (C_u=53 %) with dry irrigation season leads to maximum yield losses (Figure 5-b) due to reduced crop productivity over the furrows' tail (Figure 6-a). When I=0 yield losses are minimal (less than 4 %) if K_{nun}=0 and C_v=0.

2. Pollution of ground water:

Variation of irrigation depth and fertilisation rate across the furrow set might provoke pollution of ground water. Drainage and N-leaching relative to May-September period are uniform and harmless for environment in case of moderately wet irrigation season (P_I = 77%) under any of the studied irrigation/fertilisation treatments (Figures 7, 8 and 9). Mean N-leach is between 1 and 4 kg N/ha in average and dry irrigation seasons under "low uniform" irrigation scenario (I = 0; K_{nun} = 1; C_u = 53 %) (Figure 7-a). The drier is the irrigation season the higher is risk to environment due to nonuniformity in irrigation water distribution and N-broadcast. Standard deviation bars (STDEV) augment and reach 100 mm for the drainage and 4-5 kg N/ha for the leaching in the very dry 1987 of P_I = 3%. The same holds true for the residual N-NO_3 in the soil (Figure 7-b) when STDEV reaches 50-60 kg N-NO_3/ha after dry irrigation seasons (P_I = 3-11%).

Nonuniformity in fertilisation produces additional threat to environment when combined with the studied irrigation scenarios. Mean residual soil N-NO_3/ha reaches the maximum of 70-80 N-NO_3/ha due to the integral effect of non-uniformity in irrigation (C_u = 53 %) and fertilization (C_v = 30 %) and dry irrigation season (Figure 7-b) that is 10-15 kg N-NO_3/ha higher that that relative to the uniform scenario (C_v = 0 %). As a consequence, pick N-leaching could occur in case of precipitation extremes in fallow state (Figure 6-b). Nonuniform fertilisation results also in variable and higher N-leach in wet vegetation season (P_I = 97 %) when rainfed maize is grown.

3. Mitigation of adverse impact on environment

Adverse impact of furrow irrigation on productivity and environment is mitigated by improving "inter-row" nonuniformity both of stream advance (to K_{nun} < 0.5) and N-broadcast (to Cv < 10%) while maintaining soil moisture above the soil cracking threshold on a regular basis. For that purpose application of environmentally sound water saving irrigation technologies, such as "surge" and "cut-back" irrigation or pre-seasonal compaction of the "high intake" furrows, are recommended. That reduces 2-3 folds STDEV bars of drainage, N-leaching and residual N-NO_3 in the soil when I = 0 (Figure 8). Application of 50 % more irrigation water (I = 0.8), that minimises yield losses, is not sustainable option for environment (Figure 9). In that case 37-45 % of irrigation water and 10-12% of applied nitrogen fertiliser are lost by deep percolation.

Developed scenarios of nonuniformity of irrigation water and nitrogen fertiliser distribution over a furrow set are applicable for any soil. Obtained results about yield losses due to irrigation and fertilisation nonuniformity and climate variability as well as associated environmental impacts are valid for a precise irrigation scheduling relative to the soils of medium water holding capacity and permeability in Sofia field. Adverse impacts to environment and yield losses in irrigation practice could be even more profound than those simulated in this study.

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- Atanassova, I., S. Doerr, 2010. Organic compounds of different extractability in total solvent extractsfrom soils of contrasting water repellency. European Journal of Soil Science, 61, 298-313.
- Schwesig, D., A. Göttlein, L. Haumaier, R. Blasek, G. Ilgen. 2013. International Journal of Environmentaland Analytical Chemistry. URL: http://dx.doi.org/10.1080/03067319908032668.
- Calderón, H. W. 1982. The content and composition of humus in arid alluvial soil of Peru. Soil Science,Academy of Sciences of USSR, Moscow, 8, 53-59. (in Russian)
- Sparks, D. L. 2002. Environmental Soil Chemistry, 2nd Edition, Academic Press, San Diego, CA
- Sparks, D. L., Huang, P.M. 1985. The physical chemistry of soil potassium. p. 201-276.
- In R.E. Munson (ed.) Potassium in agriculture. Soil Science Society of America, Madison, WI.
- Noyes, J. S. 2013. Universal Chalcidoidea Database. World Wide Web electronic publication. Last update 29 August 2013. URL: http://www.nhm.ac.uk/chalcidoids.

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